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MEMORANDUM FOR PRS (In-House Publication)

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22 March 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-065**
Capt. Rene I. Gonzalez, "Synthesis and In-Situ Atomic Oxygen Erosion Studies of Space-Survivable Hybrid Organic/Inorganic Polyhedral Oligomeric Silsesquioxane Polymers"

Ph.D. Dissertation Defense
(University of Florida, FL, 04 April 2002) **(Deadline: 04 Apr 02)**

(Statement A)

UNIVERSITY OF FLORIDA

Chemical Engineering Department

Synthesis and In-Situ Atomic Oxygen Erosion Studies of Space-Survivable Hybrid Organic/Inorganic Polyhedral Oligomeric Silsesquioxane Polymers

DISTRIBUTION STATEMENT A
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Ph.D. Dissertation Defense
for

Capt Rene I. Gonzalez

Materials Application Branch

Space and Missile Propulsion Division
Air Force Research Laboratory

Research Advisor: Prof. Gar B. Hoflund

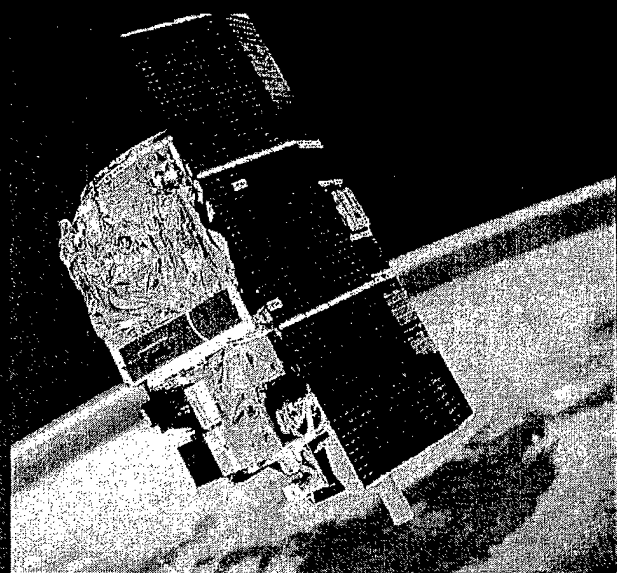
Polymeric Materials

- Cost is the variable plaguing all space missions. ($6,000 to $10,000/1b to put payload in orbit)
- Materials are one of the main drivers of cost for space missions.
- Polymers offer many advantages (lightweight, easy to process, versatility)
- However, polymers are subject to severe degradation in Low Earth Orbit space environment

LEO Environment
(Altitudes of 200 to 1500 km)

- Atomic Oxygen
  - $\sim 10^8$ atoms/cm^3
  - Formed from photo-dissociation of O_2 in atmosphere.
  - Actual flux on spacecraft traveling at 8 to 12 km/s $\sim 10^{15}$ atoms/cm$^2 \bullet$s
  - collision energy ~ 5eV
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar UV and VUV radiation
  - VUV wavelengths in LEO extend below 290nm.
  - Bond scission and radical formation can lead to embrittlement.

Goal: Develop Multi-Functional, Space-Survivable Materials (AFOSR/ER)



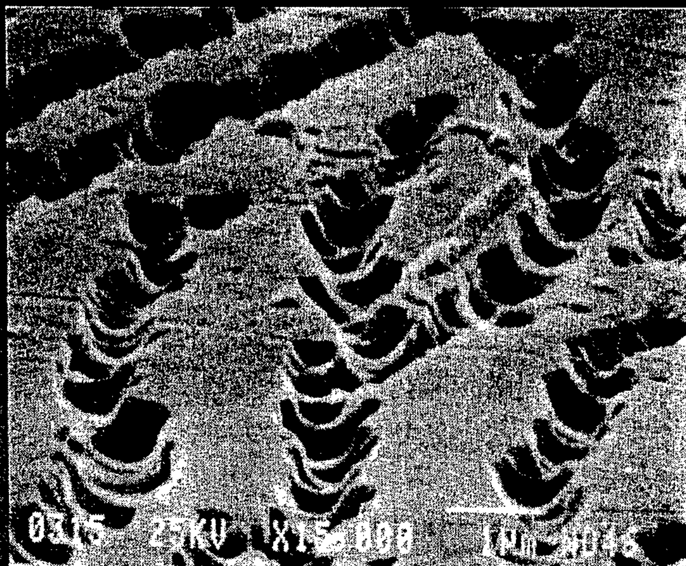
Satellites & Space Systems

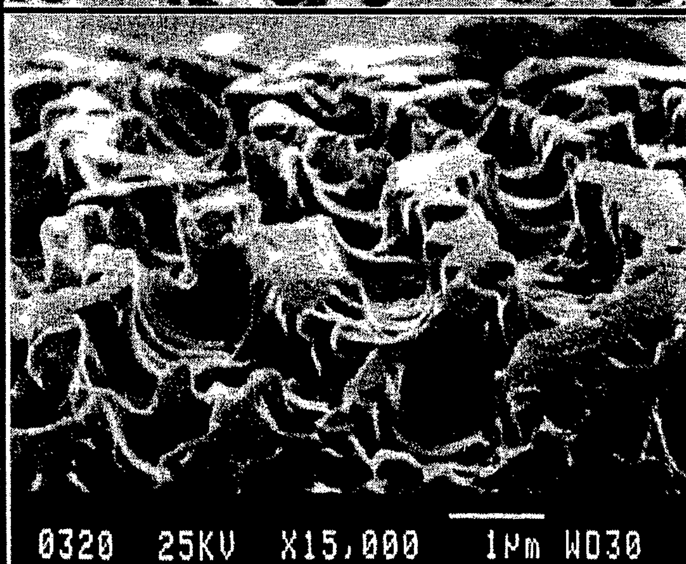
Atomic Oxygen Reaction Efficiency cm^3/atom		
Material	Rel. Rates*	LEO
Kapton	1	3.0×10^{-24}
Polyethylene	0.9	3.7×10^{-24}
FEP Teflon	<0.03	$<0.05 \times 10^{-24}$
FEP Teflon (Solar Max)	0.6	1.0×10^{-24}
Siloxane-imide block copolymers(25% /75%)	0.1	0.3×10^{-24}
Epoxy	0.6	1.7×10^{-24}

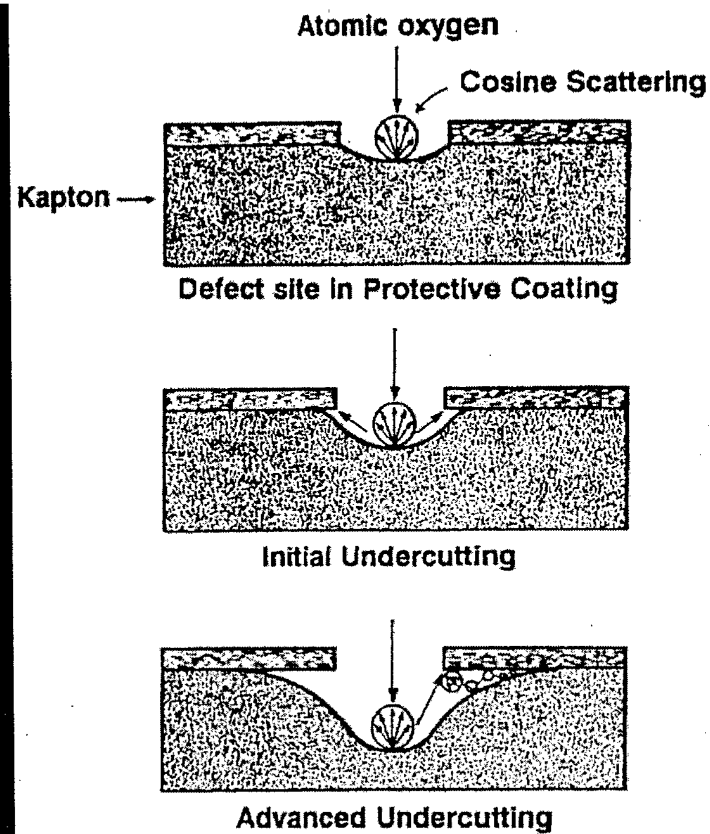
Objectives

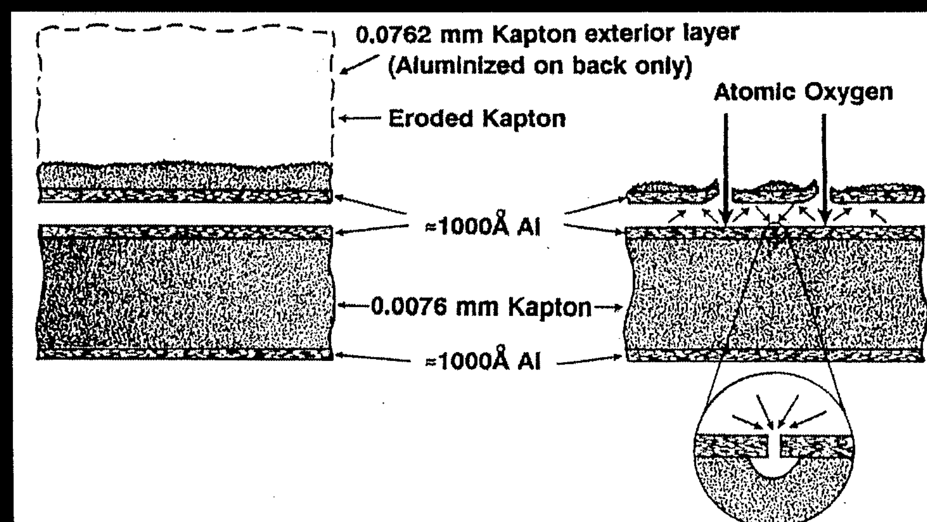
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on Hybrid organic/ inorganic nanocomposite incorporation

AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation





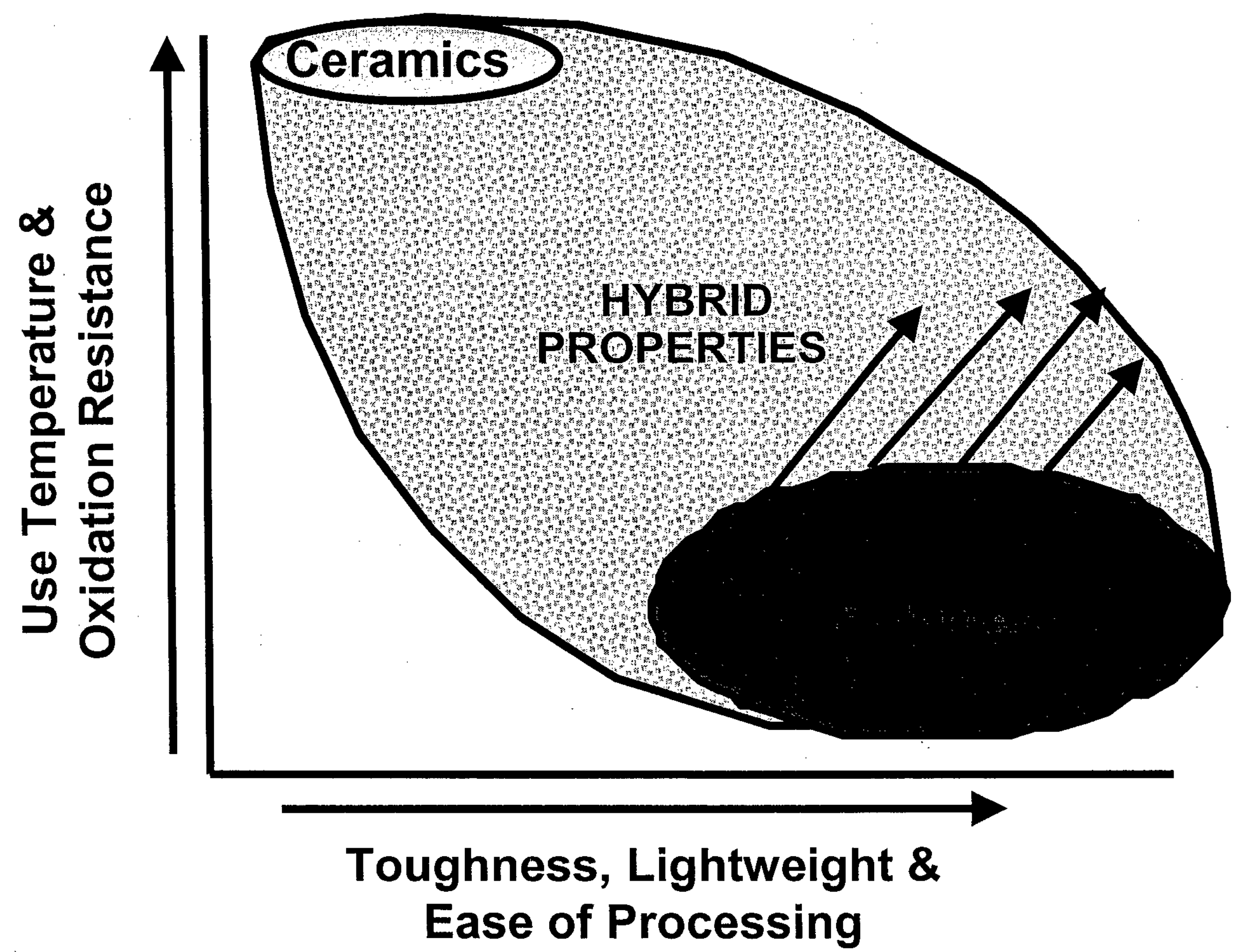




Groh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)

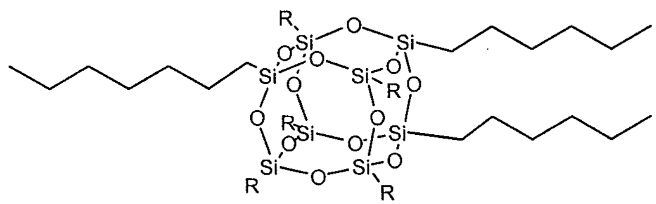
Propulsion & Space Technology is Limited by Material Properties

Goal: Develop High Performance Polymers that REDEFINE material properties

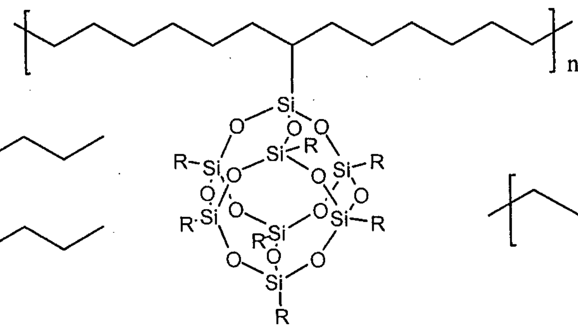


•Hybrid plastics can bridge the barrier between ceramics and polymers

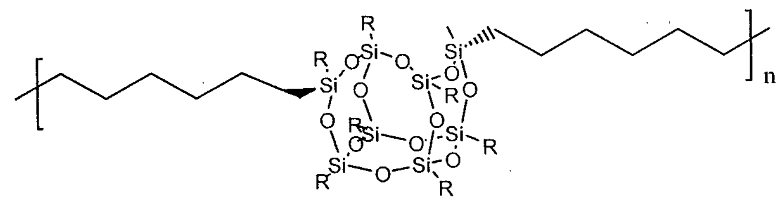
POSS Polymer Incorporation



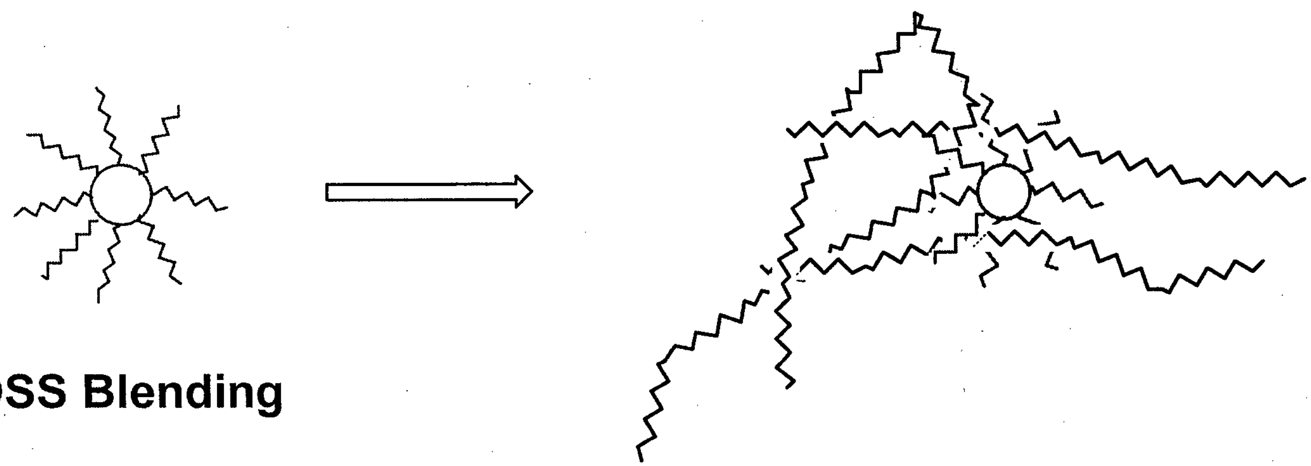
Cross-linker



Pendant Polymer

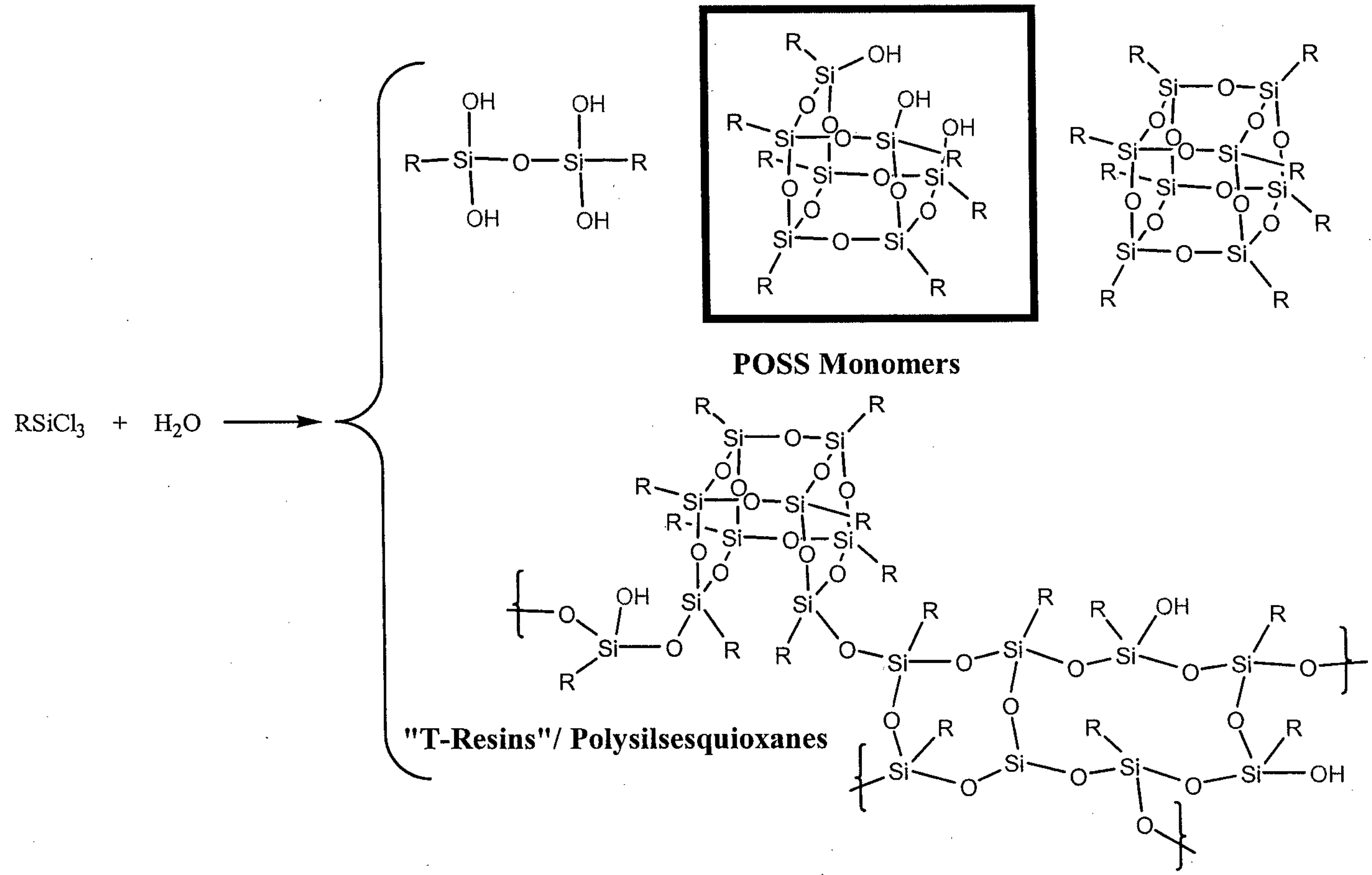


Bead Copolymer



POSS Blending

POSS = Polyhedral Oligomeric Silsesquioxane

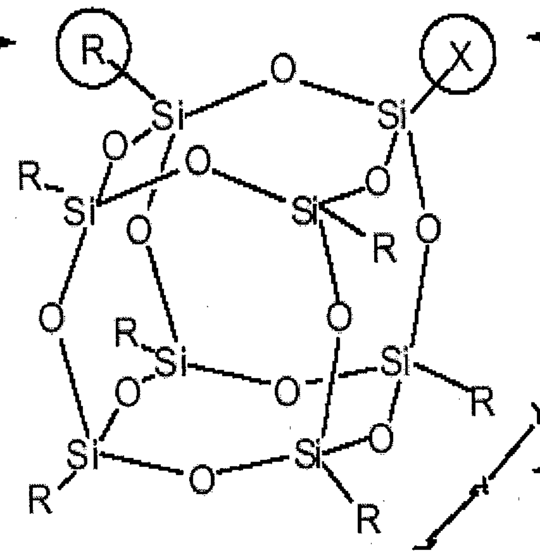


- **Traditional silsesquioxane chemistry focused on "T-Resins"**
- **The maximization of property enhancements in polymers results from interaction at the nano-level**

Anatomy of a POSS Nanostructure

Nonreactive organic (R) groups for solubilization and compatibilization.

May posess one or more functional groups suitable for polymerization or grafting.



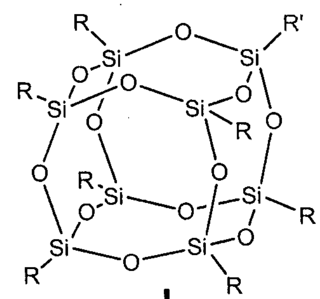
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

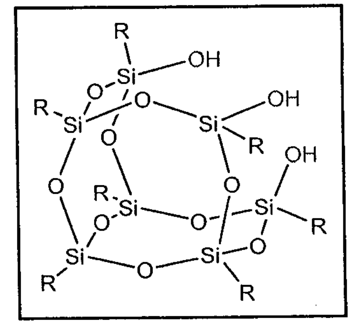
Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

POSS Monomer/Polymer Trees

Hybrid Plastics™





halides	nitriles		olefins	norbornyls
alcohols	amines	silanes	styryls	cyclopropyls
esters	isocyanates	silanols	acrylics	epoxies
acids	arylbisamines	siloxanes		
bisphenols	arydiisocyanates			
acid chlorides				
aryldiacids				

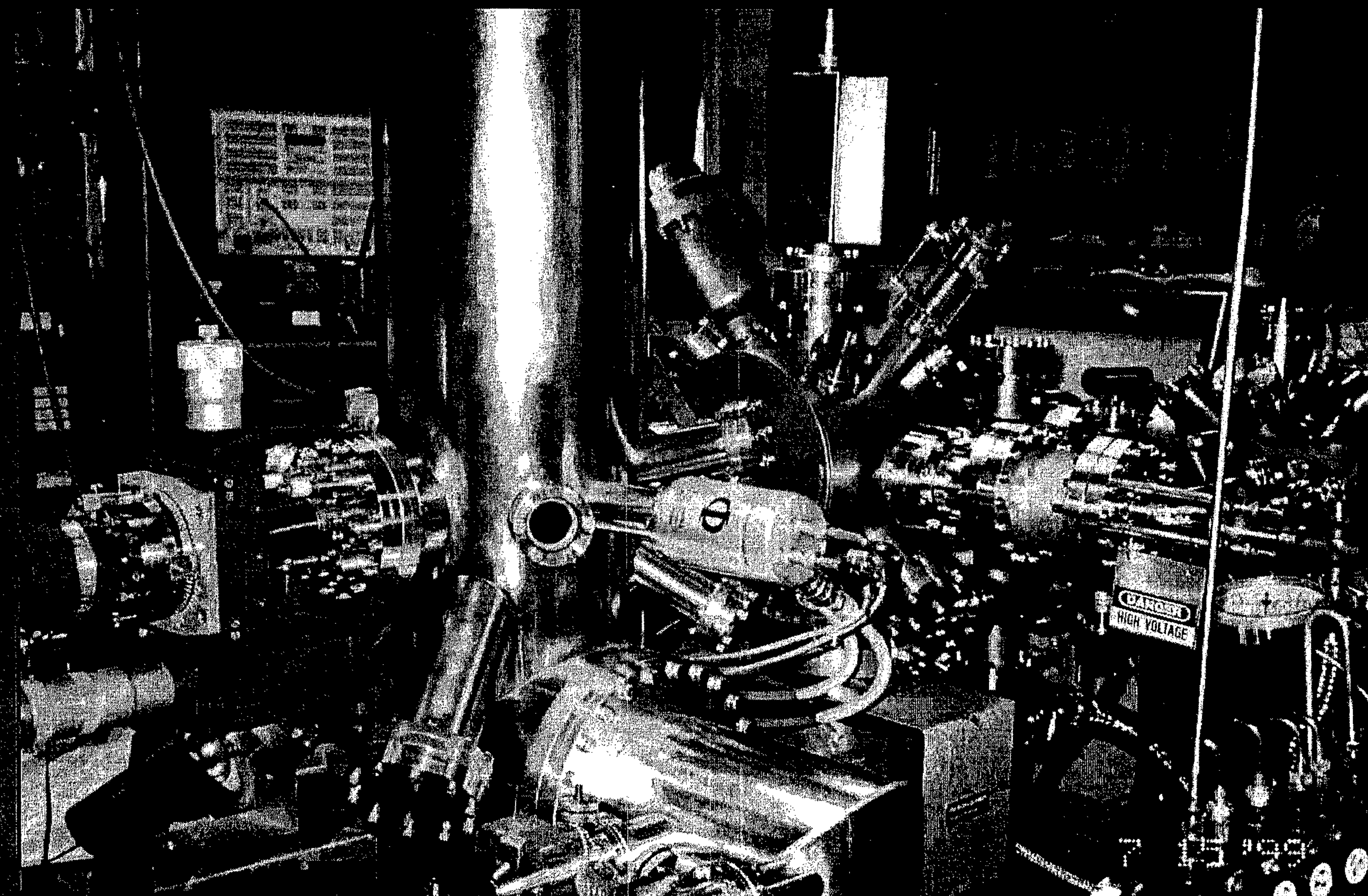
- POSS-rubber*
- POSS-urethane*
- POSS-epoxy*
- POSS-phenolic*
- POSS-imide*
- POSS-teflon

monomers and polymers.

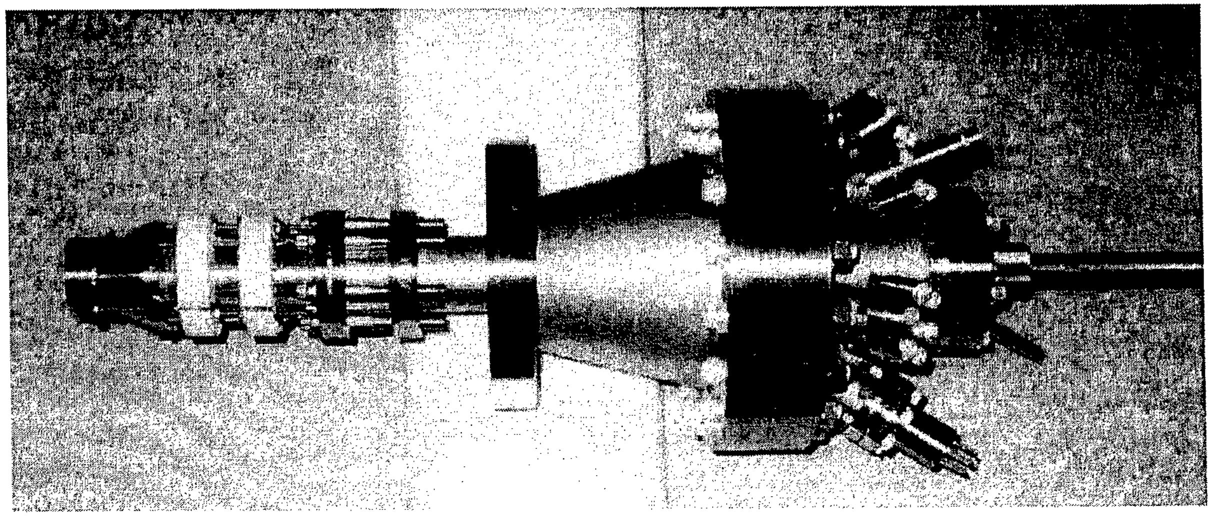
AIR FORCE RESEARCH LABORATORY

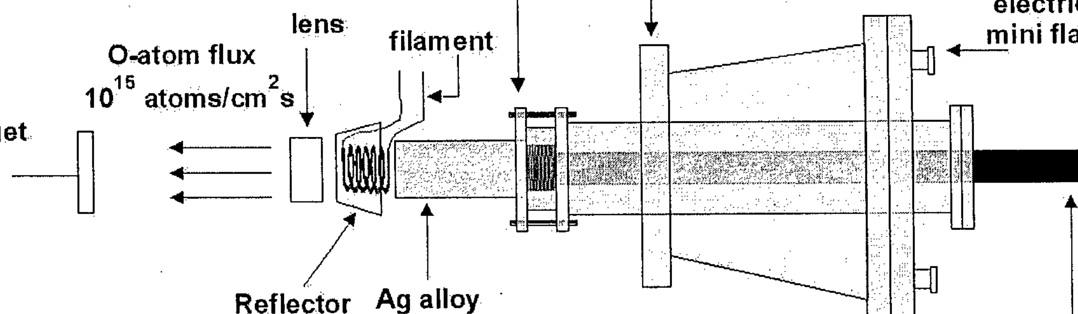
UF LEO Simulation Facility

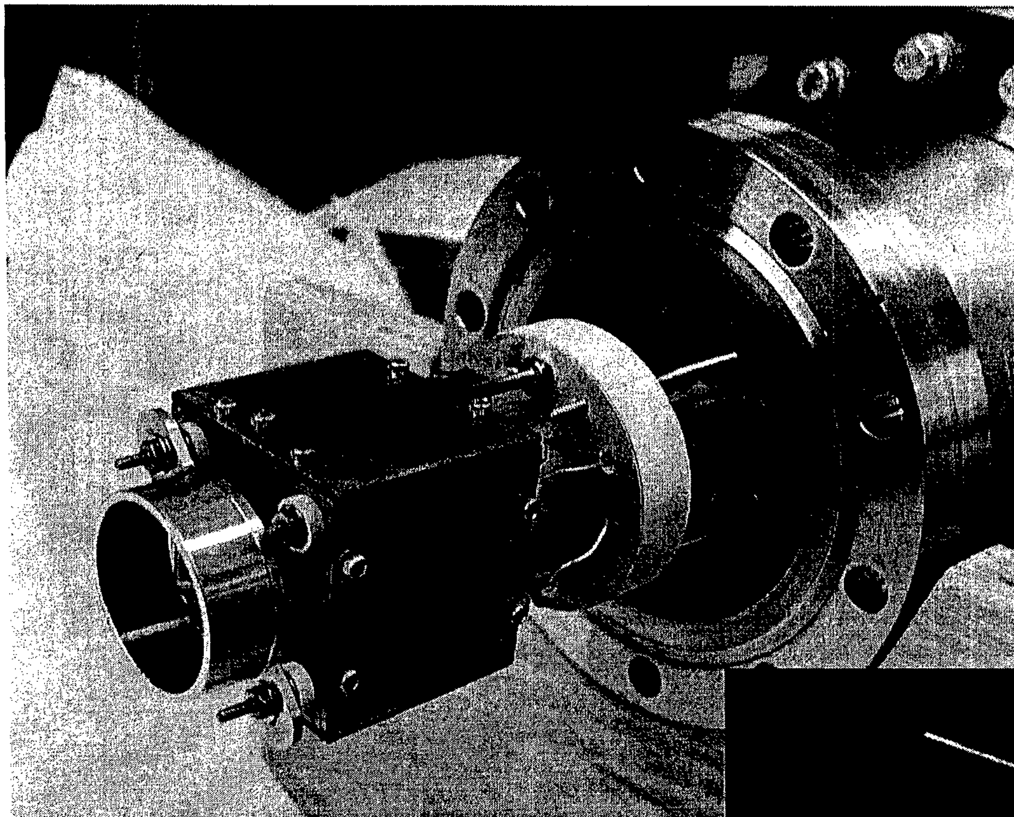
UNIVERSITY OF FLORIDA



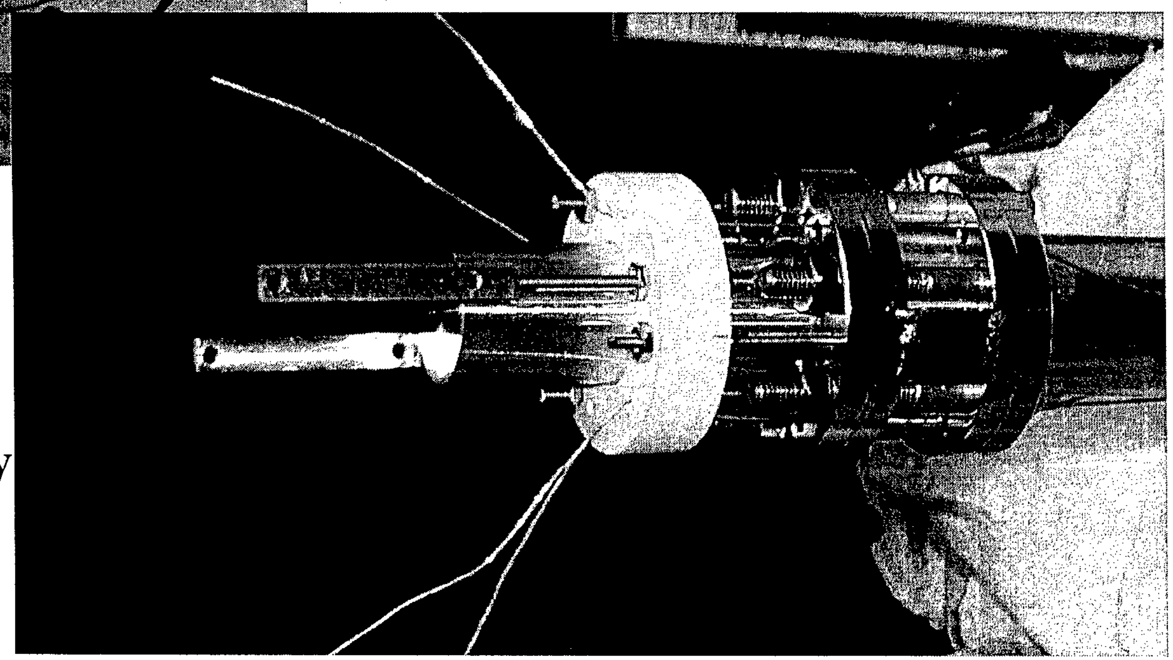
Oxygen Atom Source





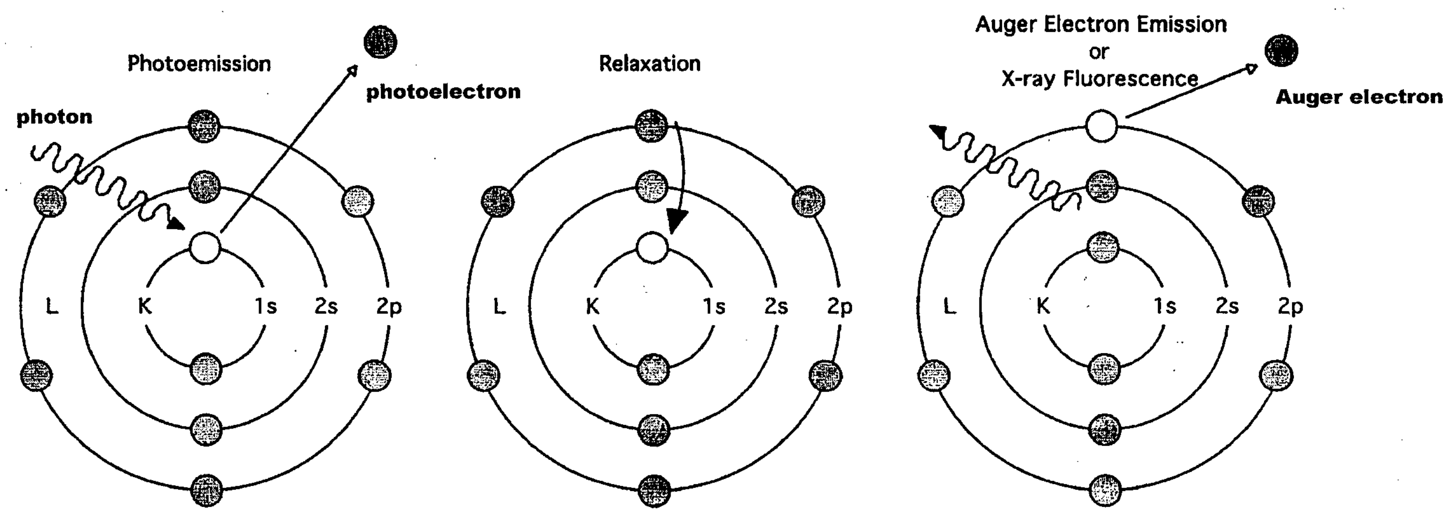


Improved reflector/lens assembly

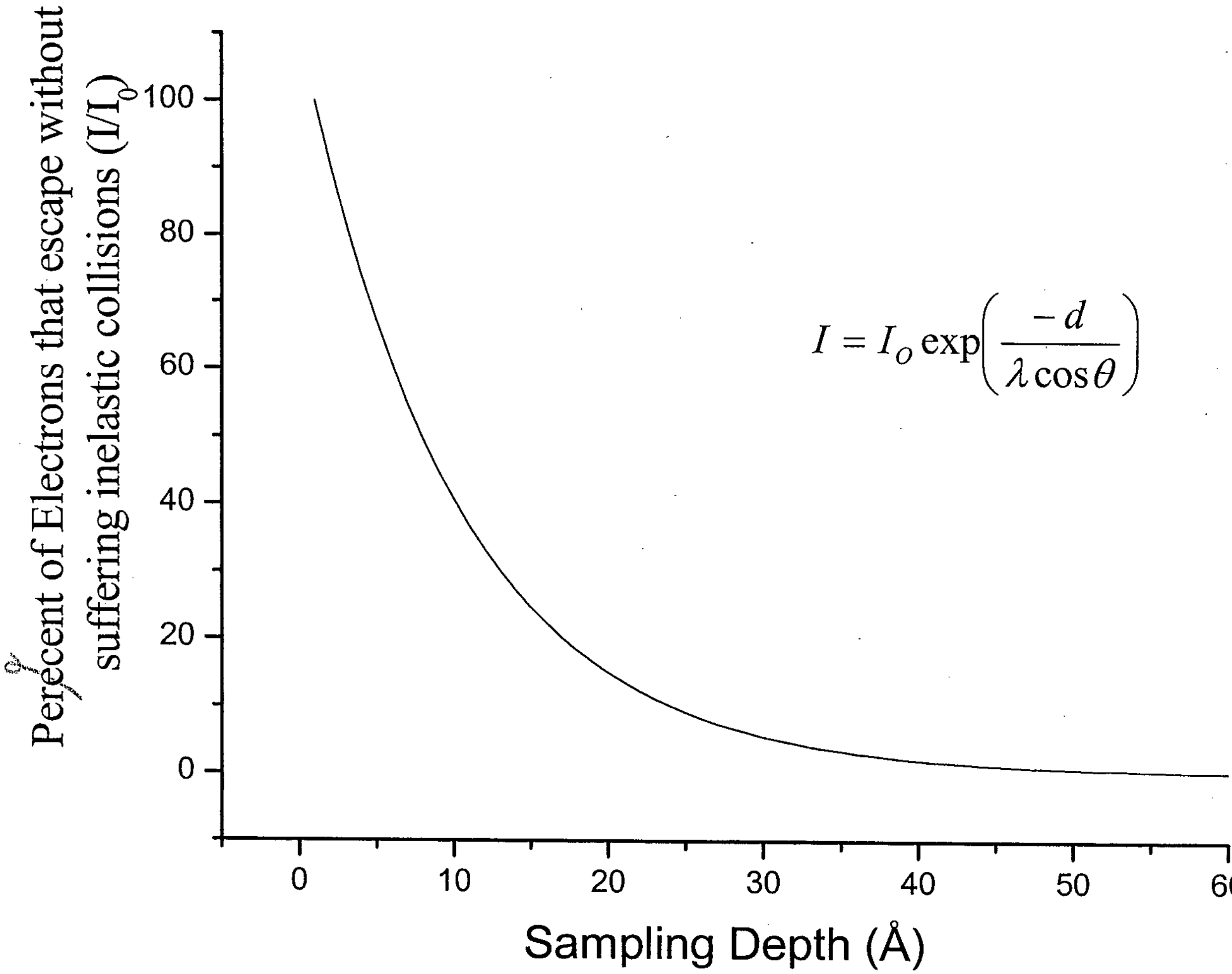


Reinforced membrane assembly

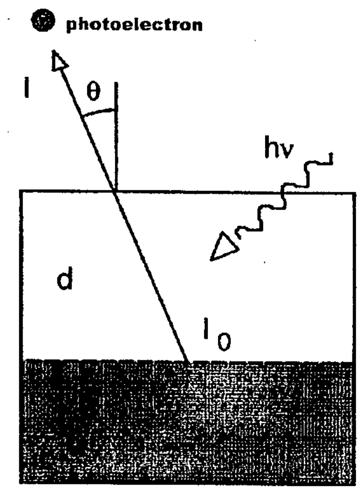
Photoemission process occurring during XPS

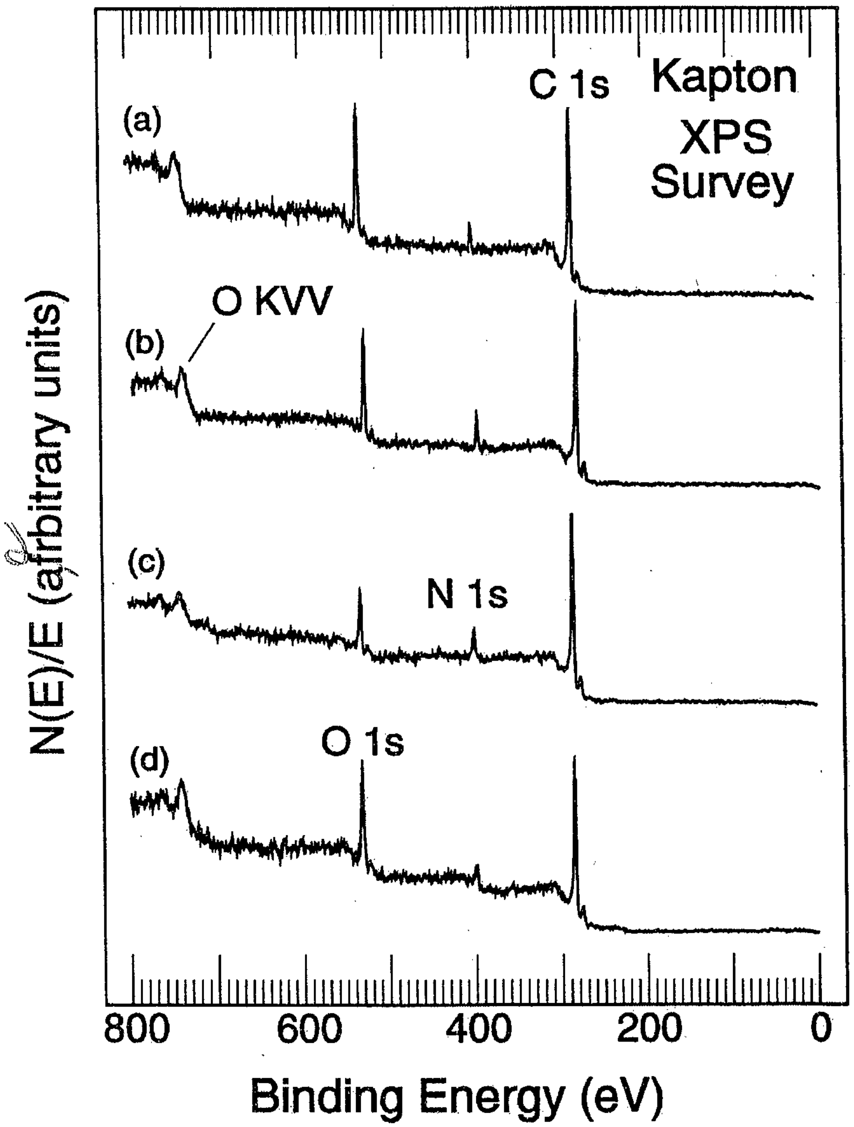


Sampling Depth of Photoelectron

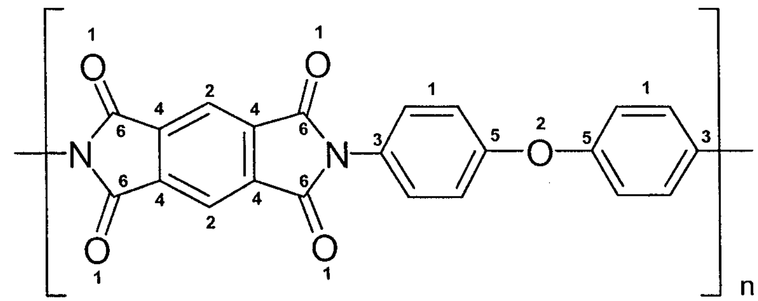


$$I = I_O \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$





Kapton

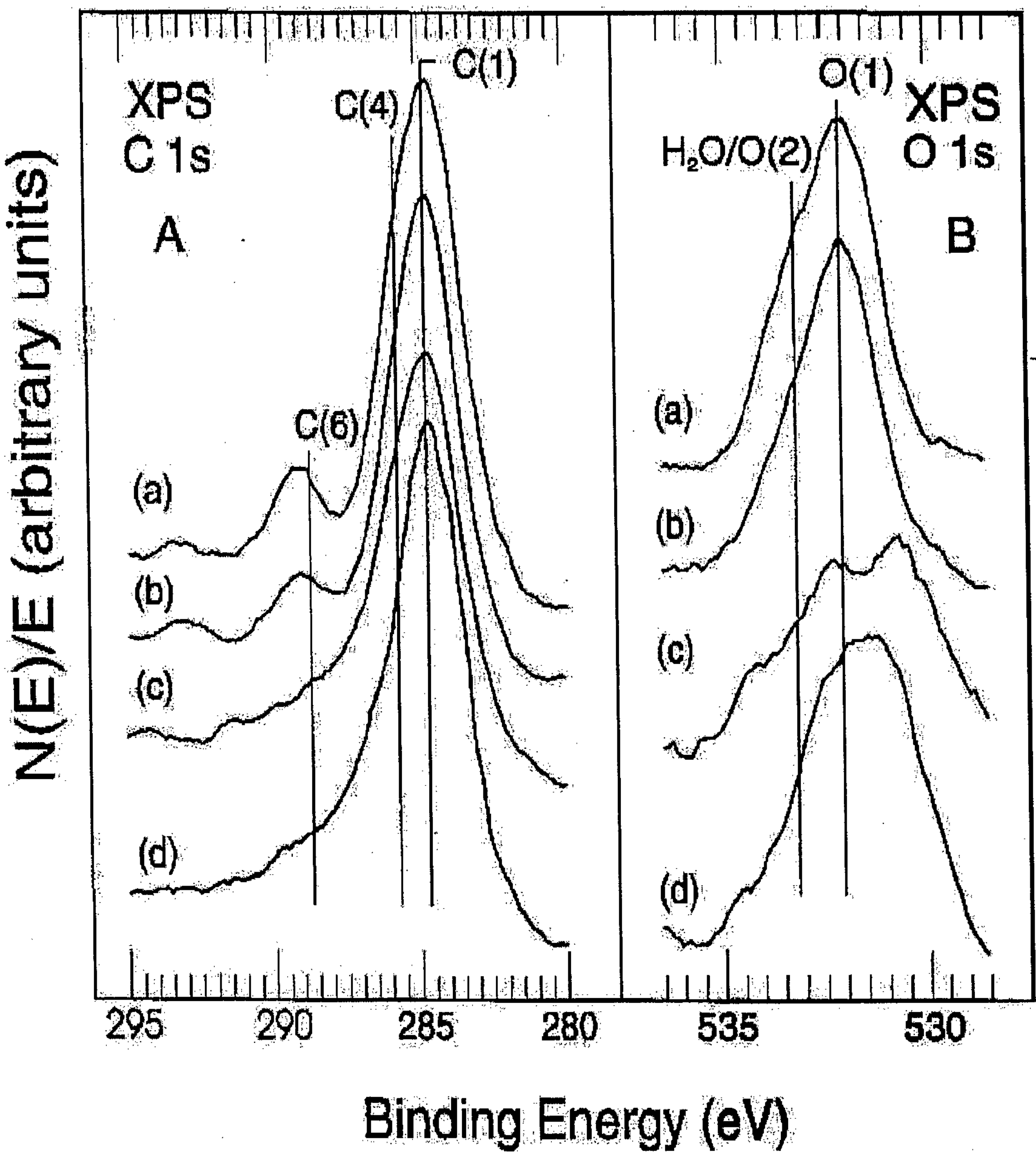


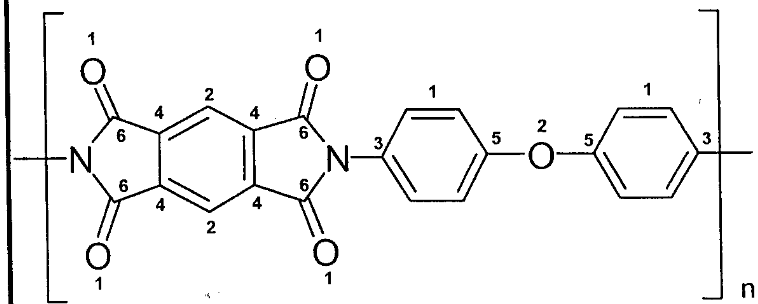
Composition, at %

Sample Treatment	O	C	N
As entered	18.1	77.7	4.2
2.0 hr	14.4	78.4	7.2
24.6 hr	9.2	83.2	7.8
3 hr in air	17.9	78.2	3.9

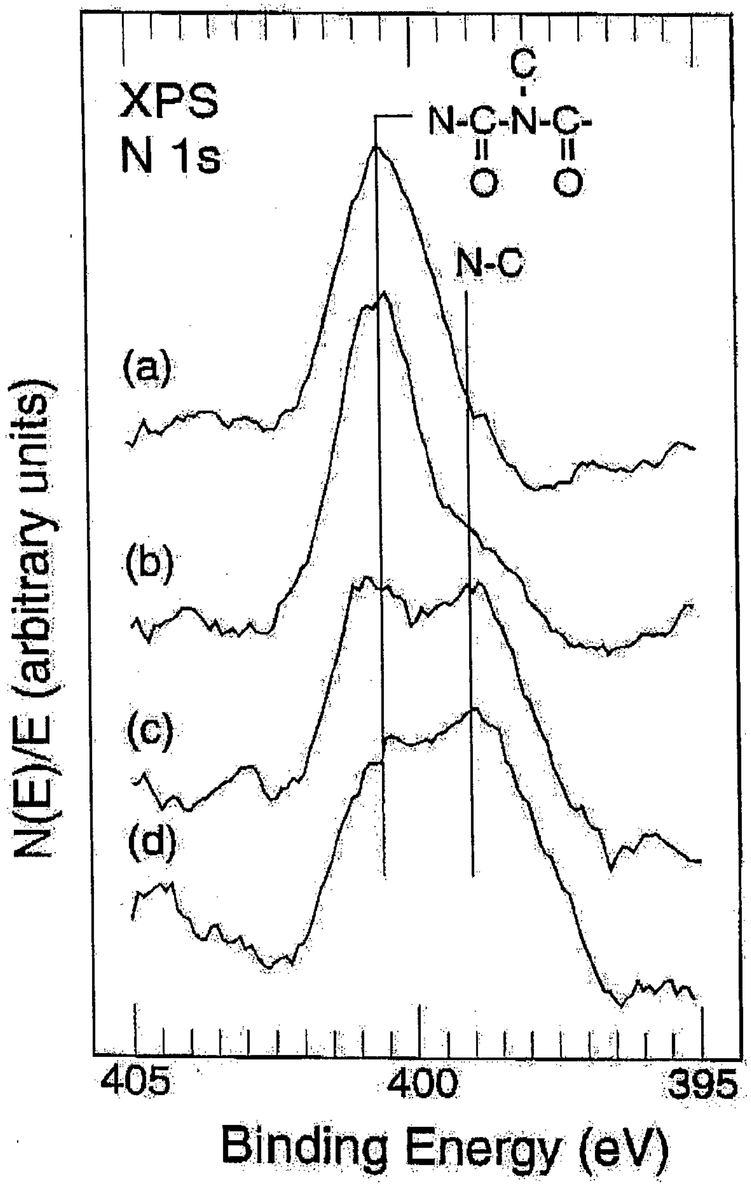
Grossman, E.; Wolan, J.T.; Mount, C.K.; Hoflund, G.B.; J. Spacecraft and Rockets, 36, No. 1, 75-78

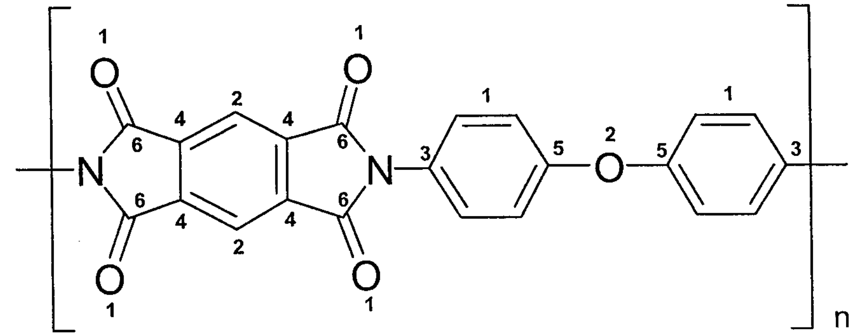
XPS survey spectra obtained from a solvent-cleaned, Kapton film after (a) insertion into the vacuum system, (b) a 20-min, and (C) a 24-h exposure to the hyperthermal AO flux, and (d) a 3-hr air exposure following the 24-hr exposure.



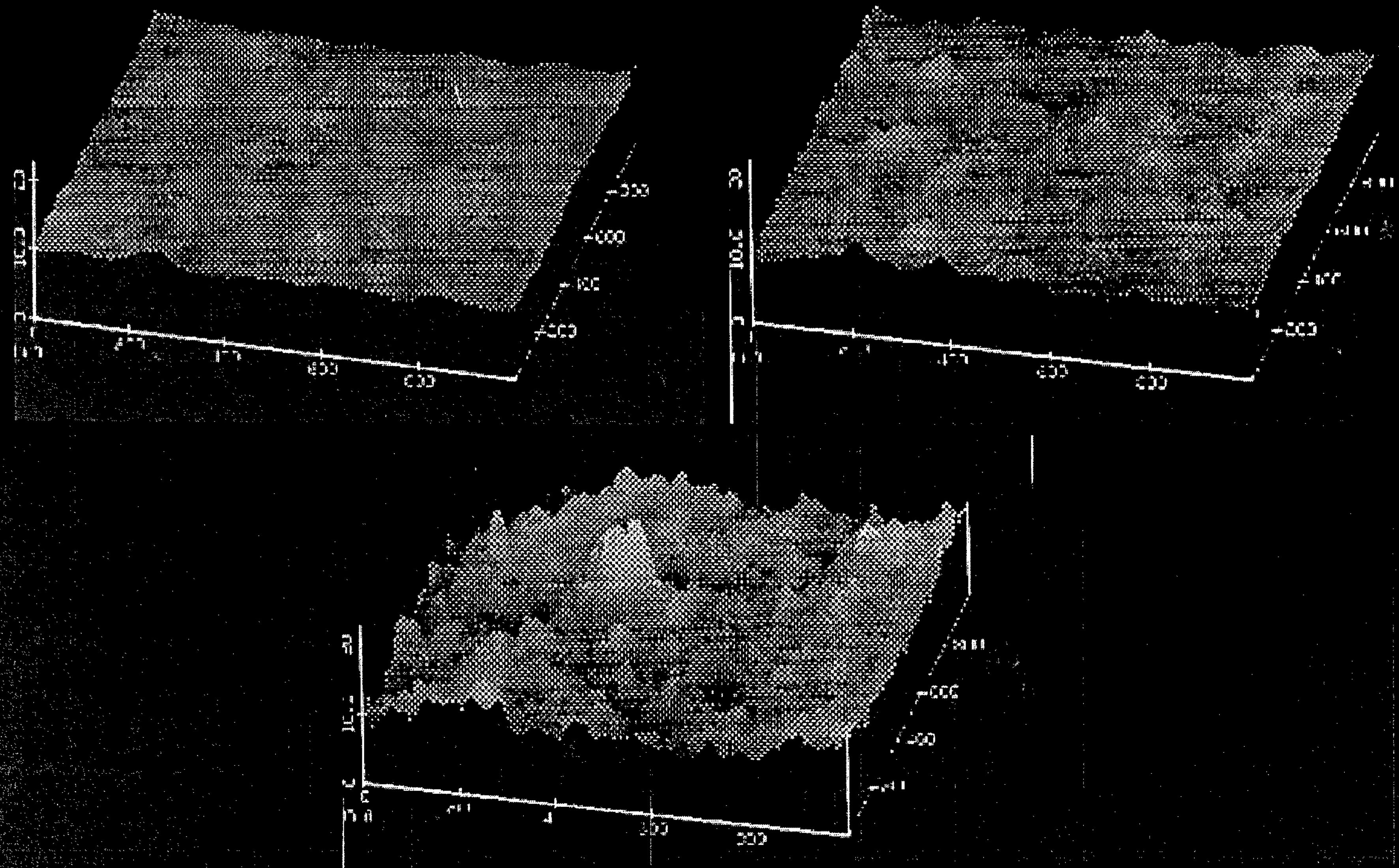


High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, Kapton film after (a) insertion into the vacuum system, (b) a 20-min, and (C) a 24-h exposure to the hyperthermal AO flux, and (d) a 3-hr air exposure following the 24-hr exposure.

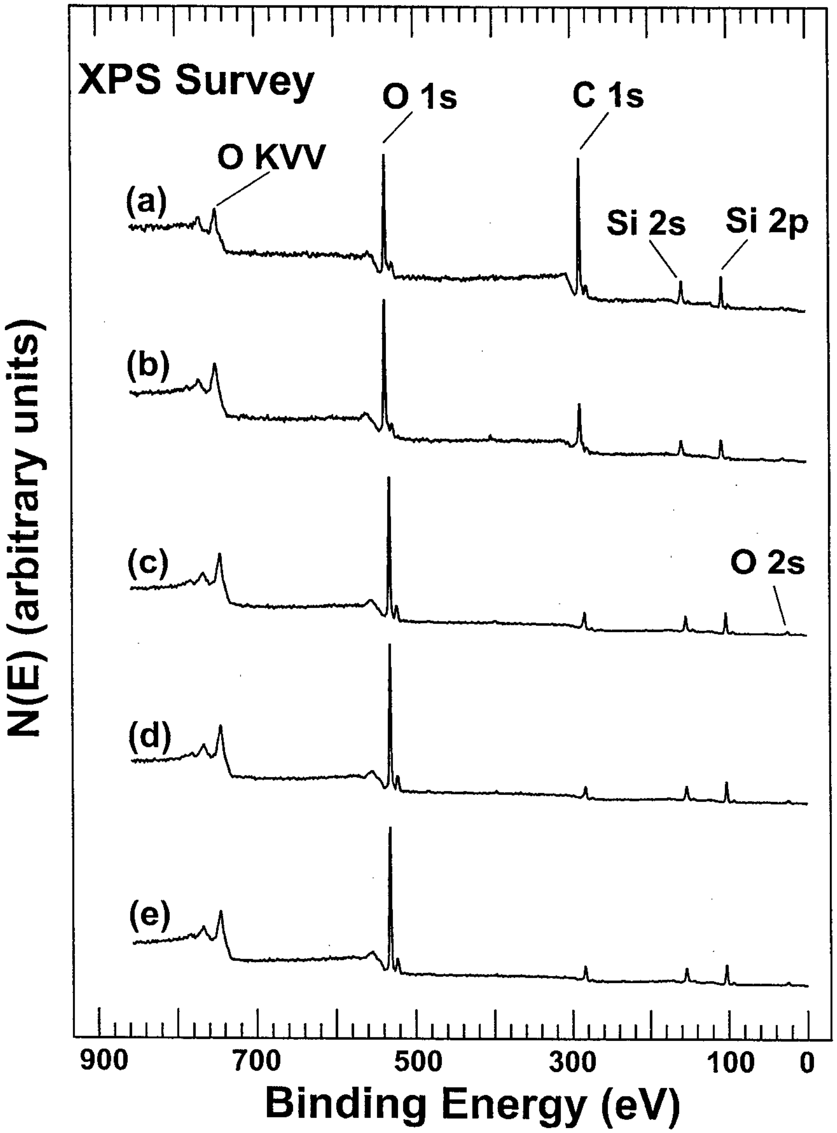




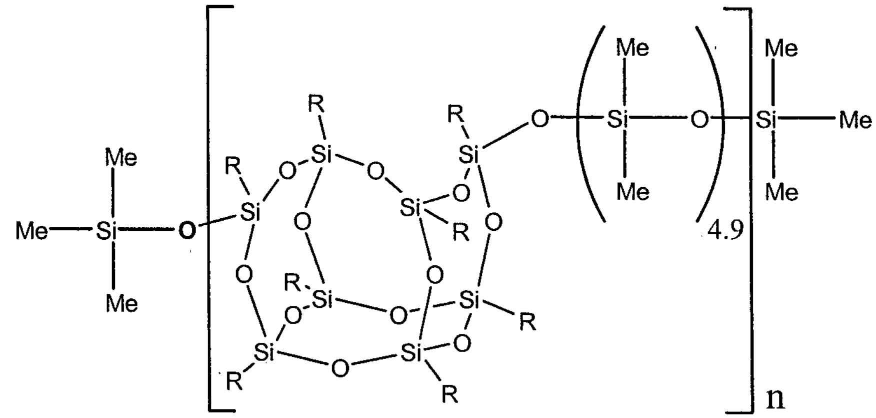
High Resolution N 1s spectra obtained from a solvent-cleaned, Kapton film after (a) insertion into the vacuum system, (b) a 20-min, and (C) a 24-h exposure to the hyperthermal AO flux, and (d) a 3-hr air exposure following the 24-hr exposure.



AFM images from a solvent-cleaned Kapton film after (a) insertion into the vacuum system, (b) a 20-min, and (c) ,a 24-hr exposure to hyperthermal AO flux.



POSS Siloxane

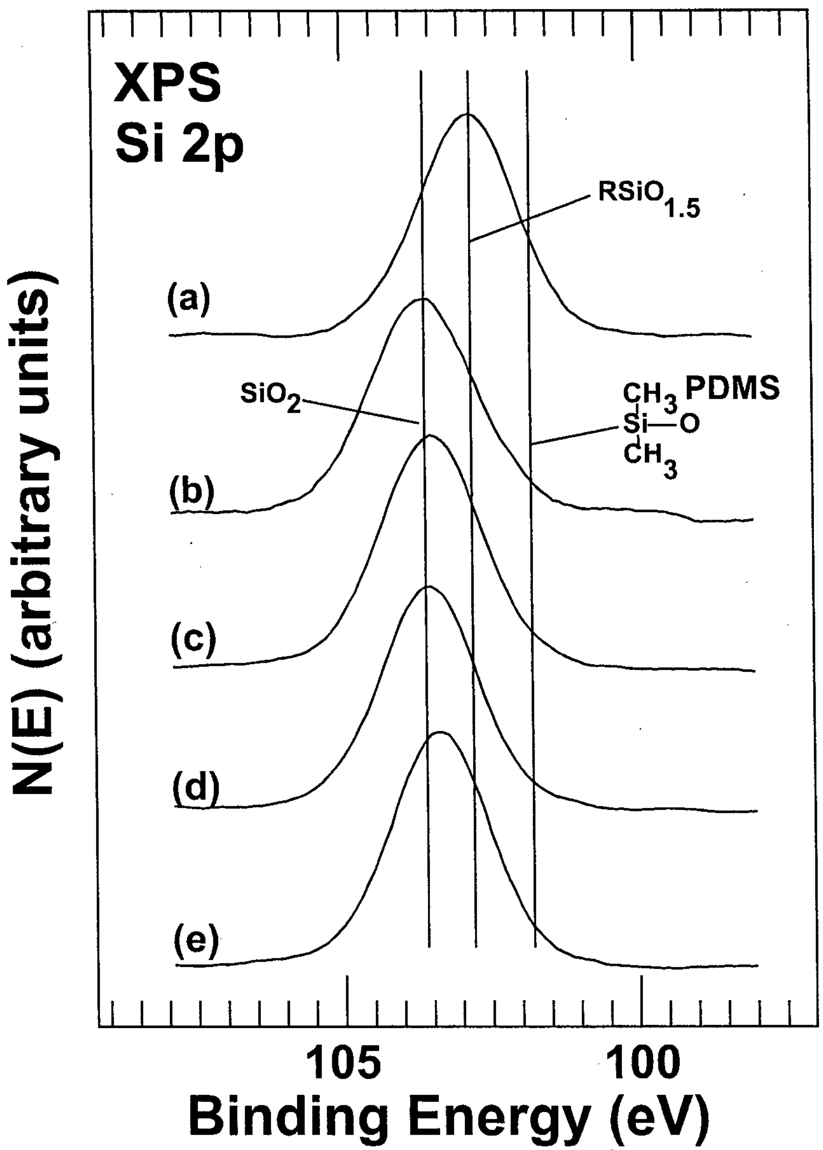


Composition, at %

Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

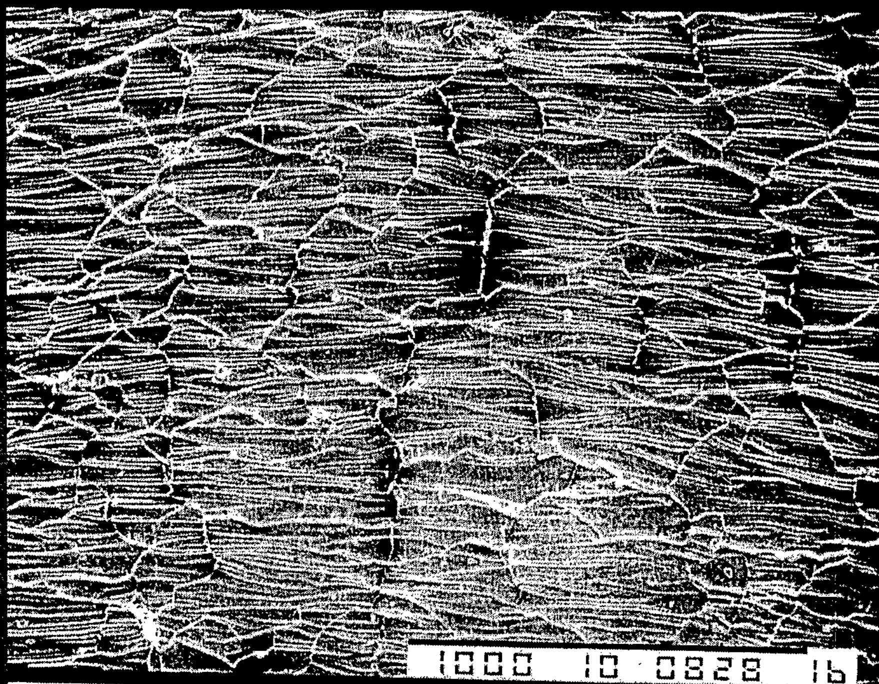
Gonzalez, R. I., Phillips, S. H., Hoflund, G. B., *J. of Spacecraft and Rockets*, Vol 37, No. 4, 2000, pp. 463-467.

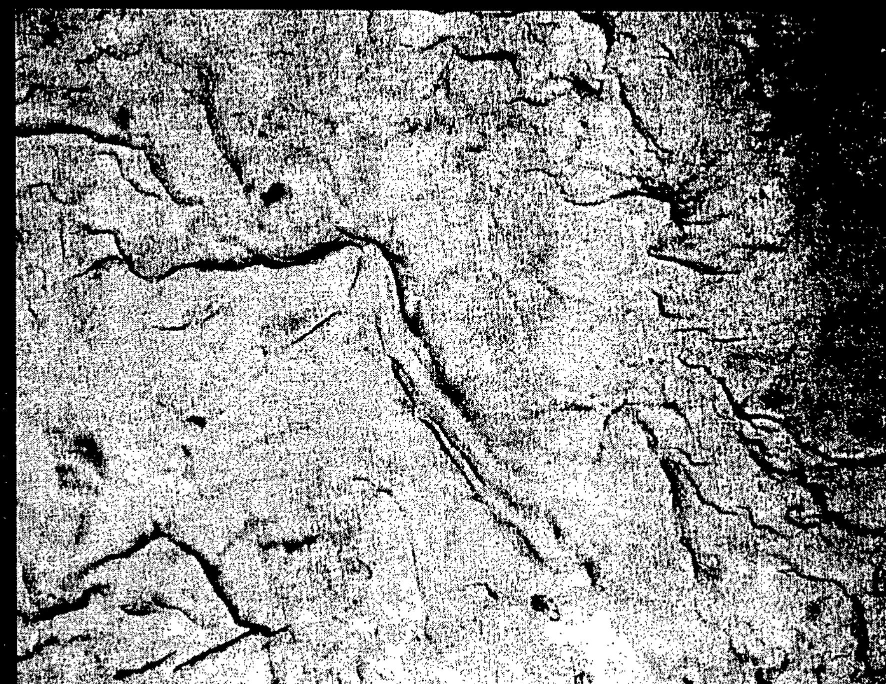
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

SEM of POSS-Siloxane Copolymer

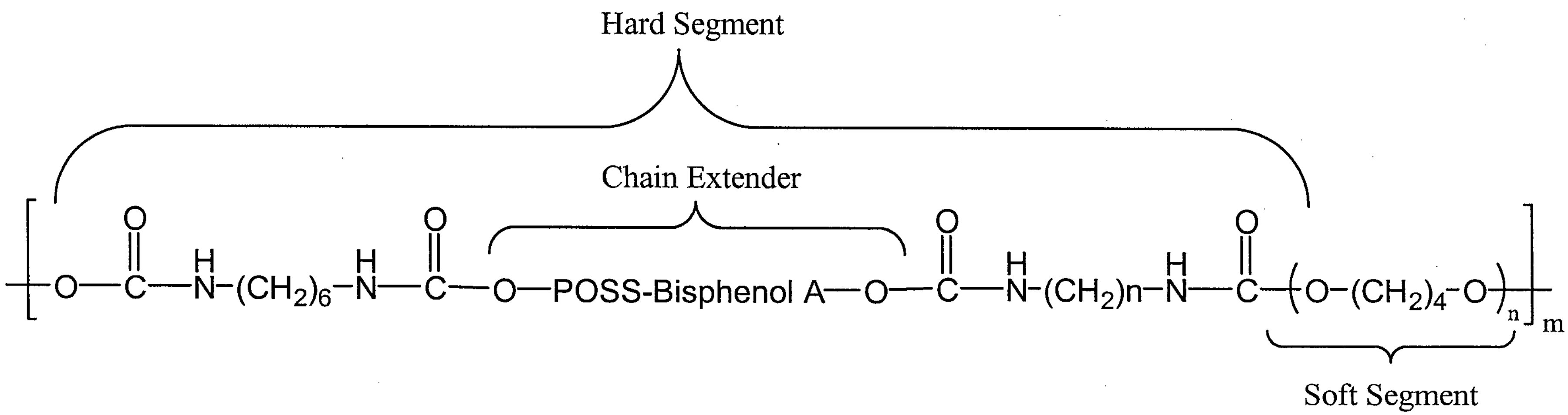




SEM of (a) unexposed and (b) exposed POSS-siloxane copolymer surfaces. The simulated LEO exposure "healed" the micro-cracks present initially in the POSS-siloxane sample.

Gilman, J.W., Shlitzer, D.S., Lichtenhan, J.D.; J. Appl. Polymer Sci., 60, 591-596 (1996)

Properties of POSS-Urethanes



Polymer	Melt Transition °C	T_{dec} °	Char Yield%	Appearance
0% POSS*	-49, 22	274 °C	1.4	Viscous Fluid
29% POSS*	201	372 °C	16.0	Solid Rubber
43% POSS*	260, 320	344 °C	20.0	Solid Rubber

Moduli for POSS BPA and TMP Urethanes

[redacted]

0 wt.% POSS	0.04 Mpa
17 wt.% POSS	0.42 Mpa
34 wt.% POSS	1.06 Mpa

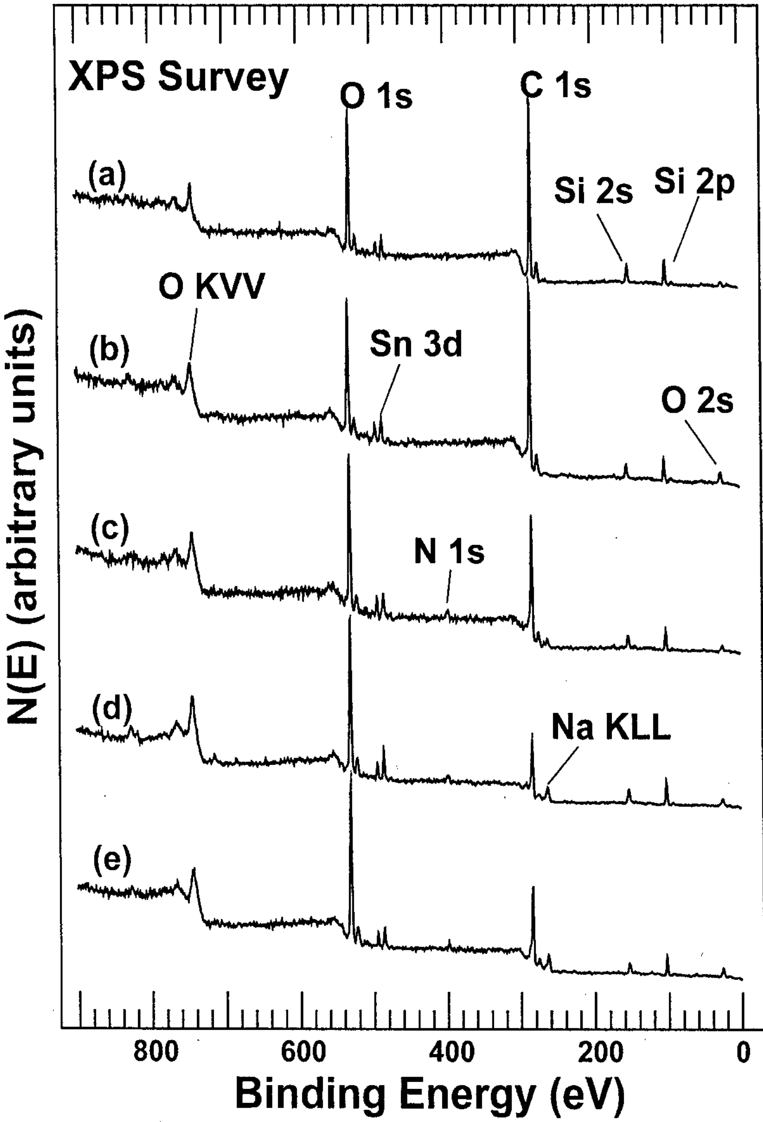
[redacted]

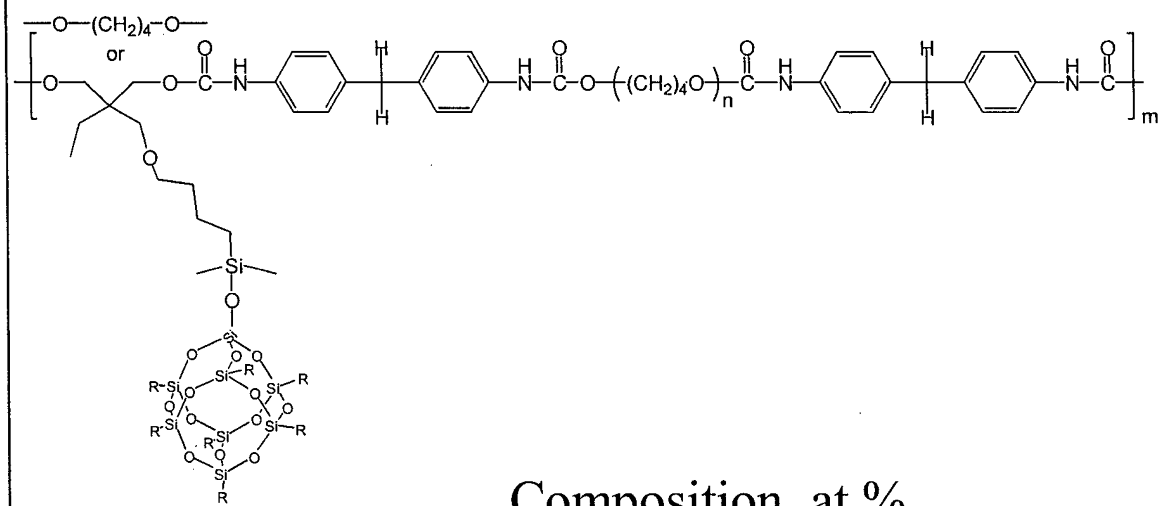
0 wt.% POSS	0.01 Mpa
17 wt.% POSS	0.14 Mpa
34 wt.% POSS	0.39 Mpa

Samples were stretched to 400% elongation

All polymers were prepared through melt polymerization

60 wt % POSS-Polyurethane



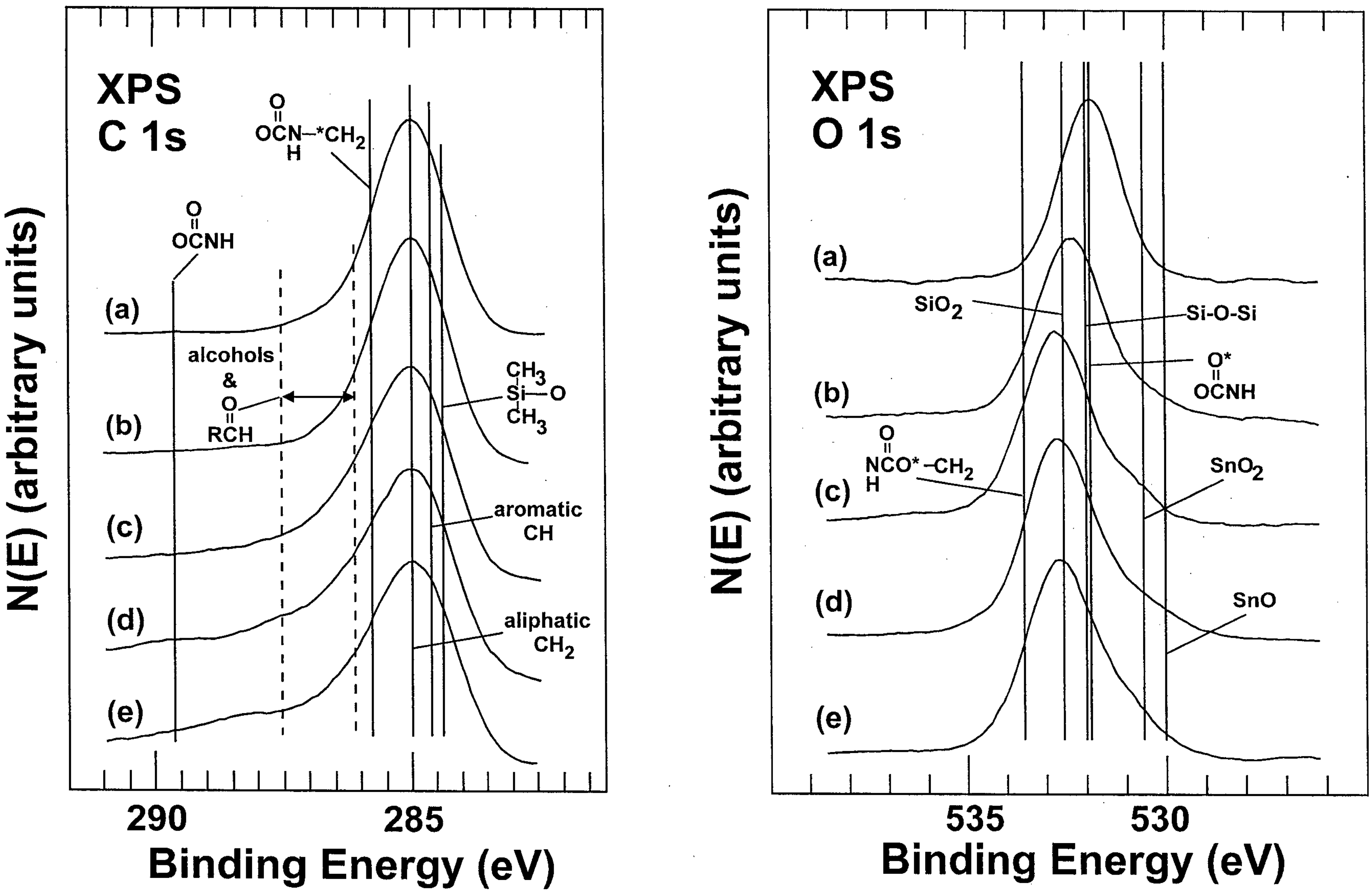


Composition, at %

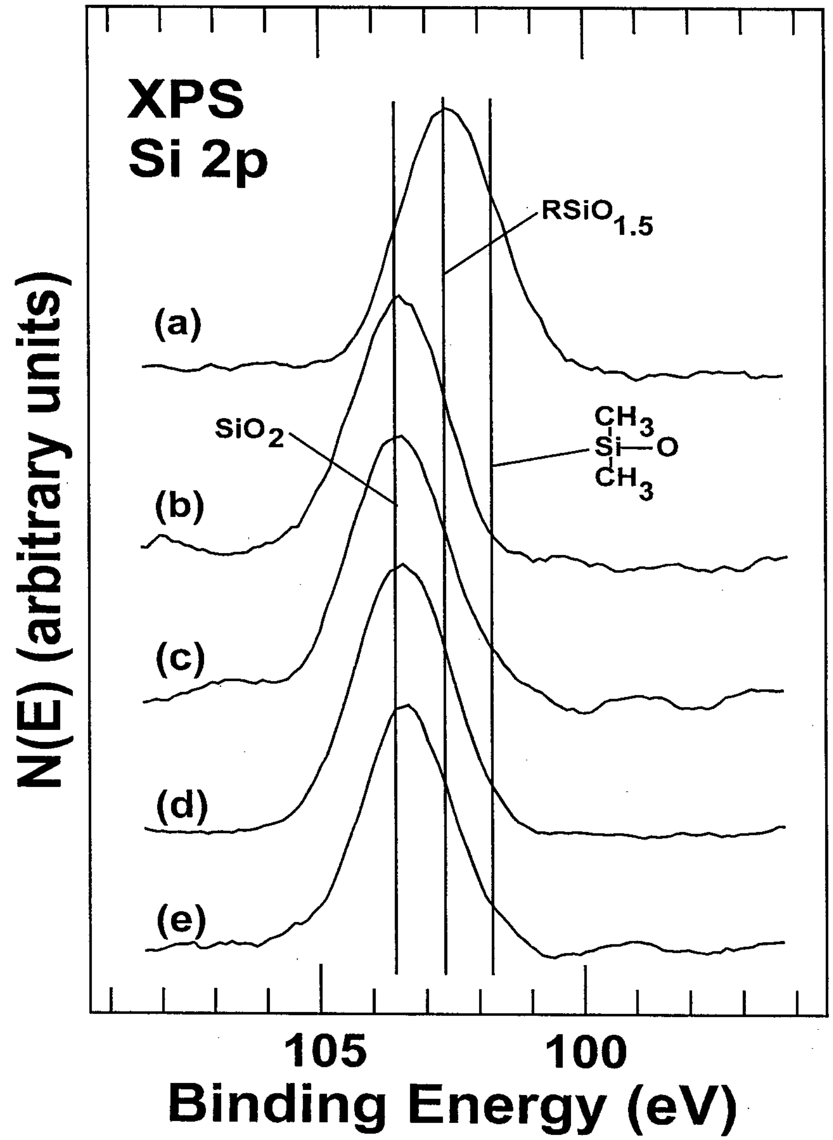
Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

Phillips, S. H., Hoflund, G. B., Gonzalez, R. I., 45th International SAMPE Symposium, 2000, Vol. 45, No. 2, pp. 1921-1931.

XPS Survey Spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

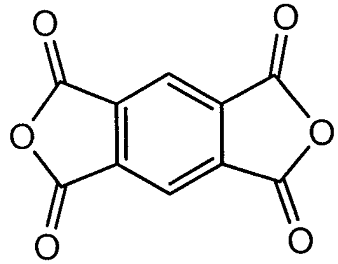


High Resolution C 1s and O 1s spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

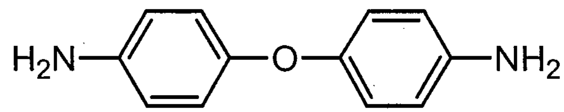


High Resolution Si 2p spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

POSS-Kapton Polyimides



PMDA



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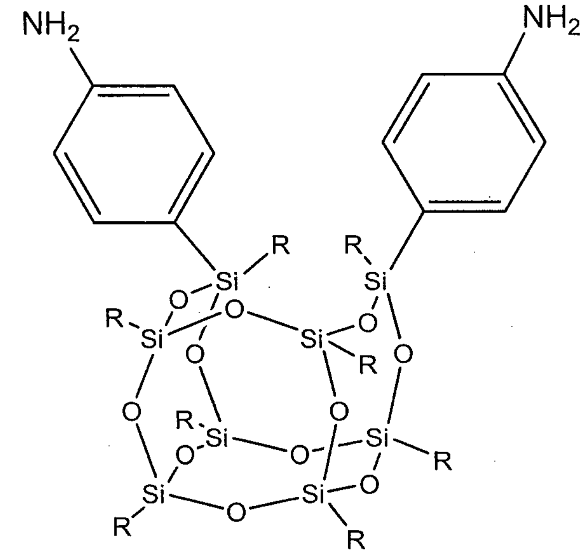
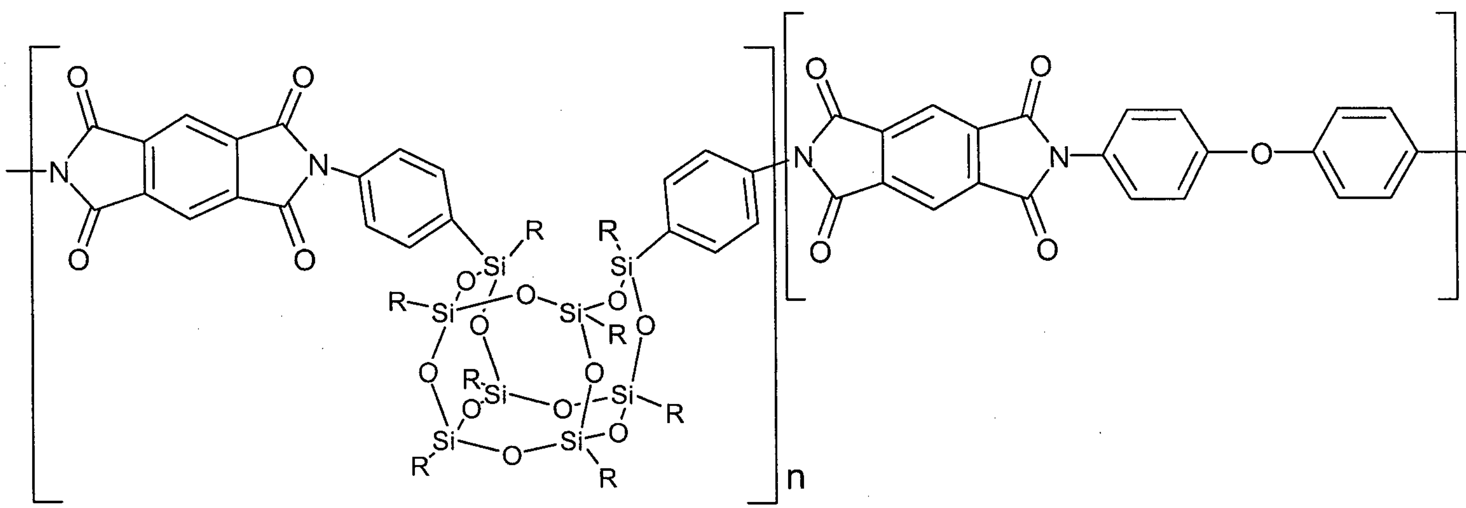




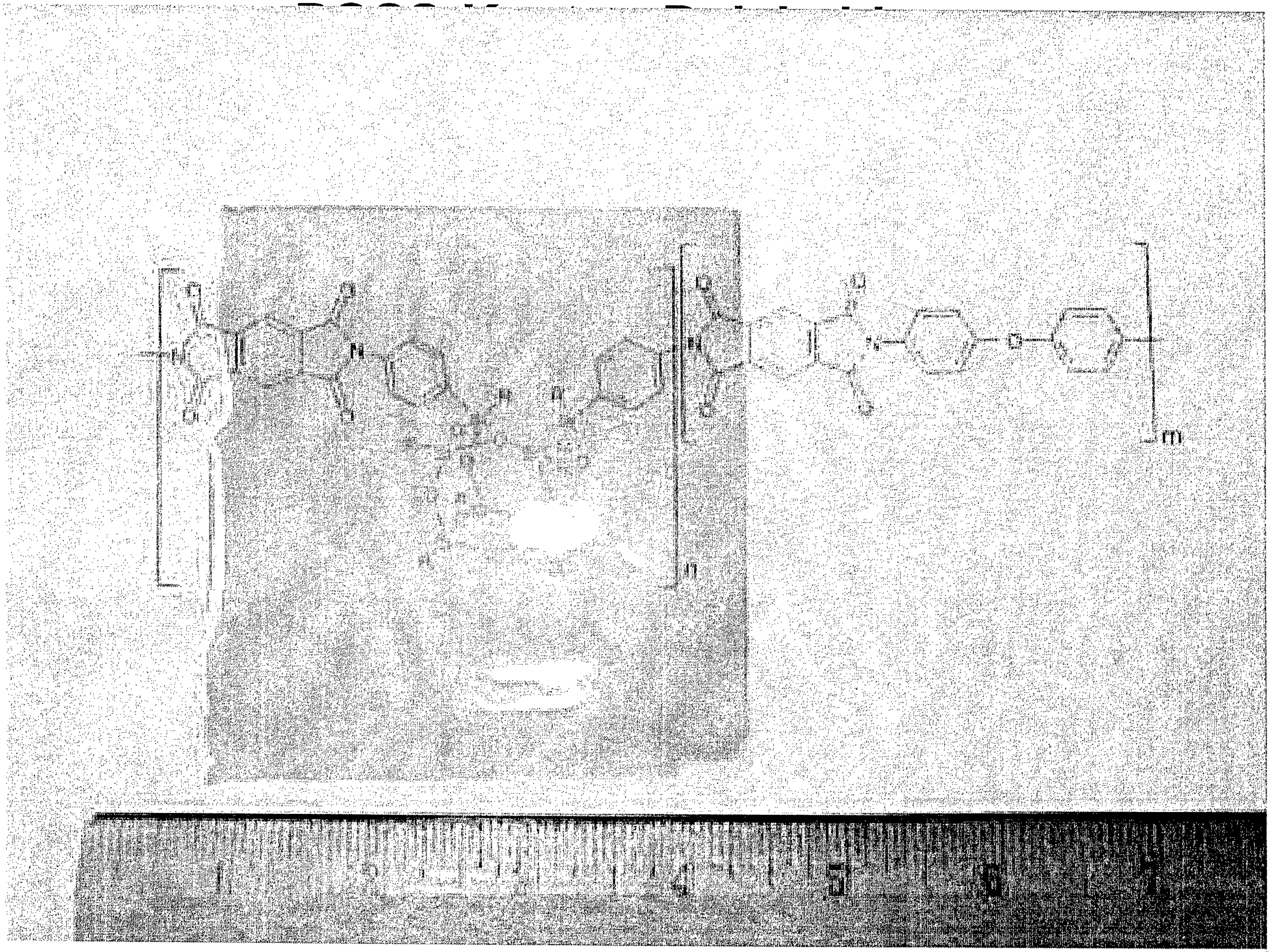


Table 2. AFRL Kapton Tensile Properties Calculated with the Average Sample Thickness.

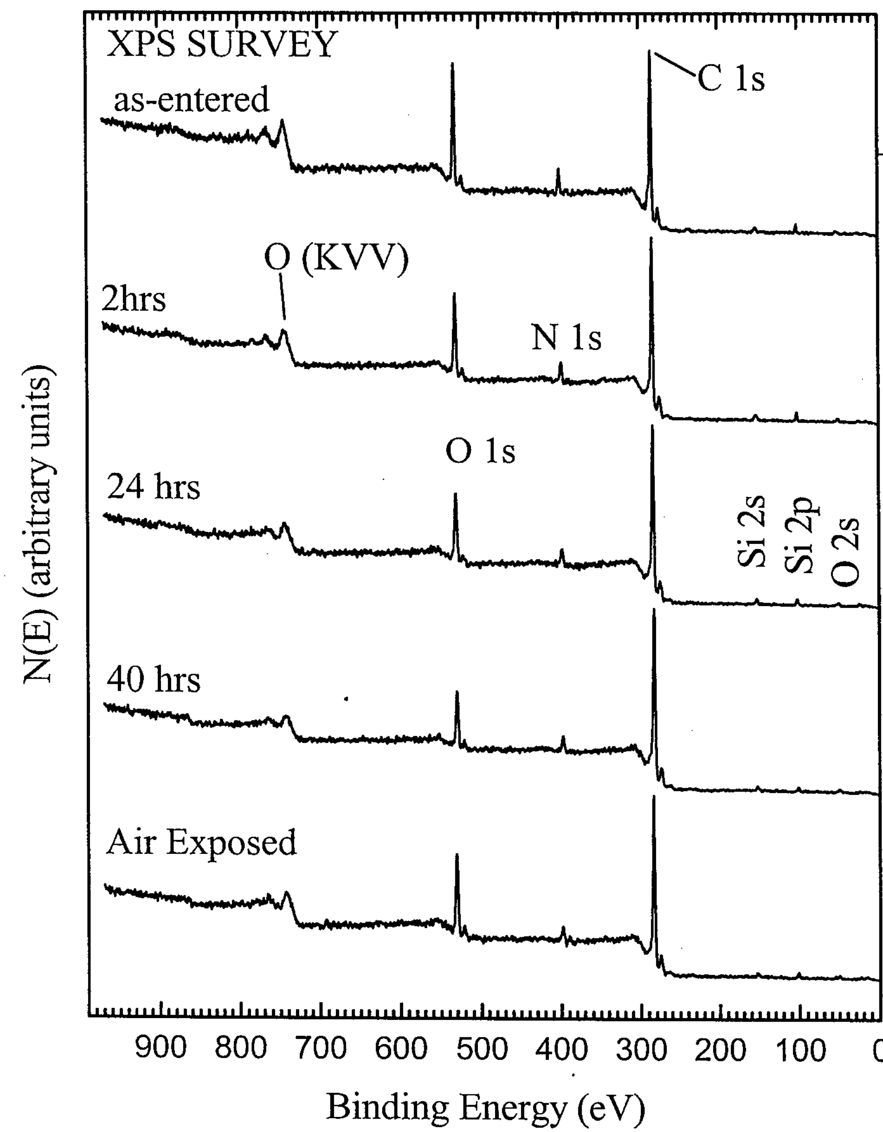
Sample No.	Young's Modulus, Ksi	Ultimate Tensile Strength, Ksi	Failure Strain, %
Baseline AFRL Kapton without POSS			
Average	348	9.0	4.86
AFRL Kapton doped with 10 wt.% POSS			
Average	370	10.8	6.59
AFRL Kapton doped with 20 wt.% POSS			
Average	321	7.5	3.89

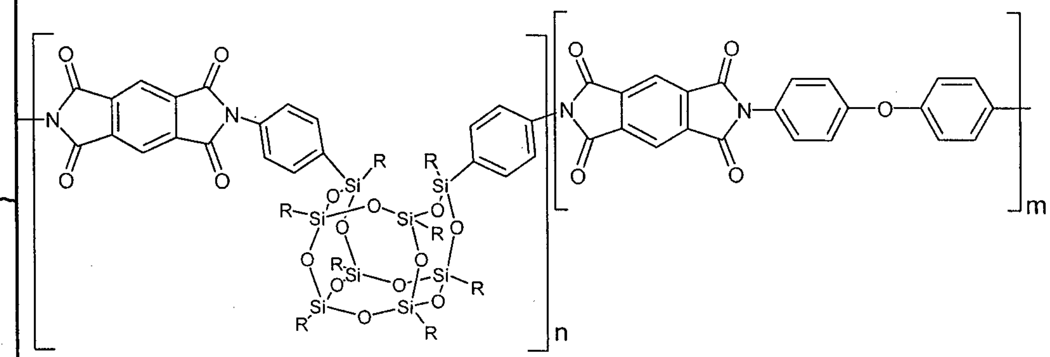
Glass Transition Temperatures of POSS-Polyimides
Measured by DMA
Heating Rate: 10°C per Minute

% POSS	Tg in Air (°C)	Tg in Nitrogen (°C)
0	386	389
10	380	381
20	370	373

Note: DuPont claims that the Tg of Kapton H is in the range of 360 - 410°C, "depending on how it is measured."

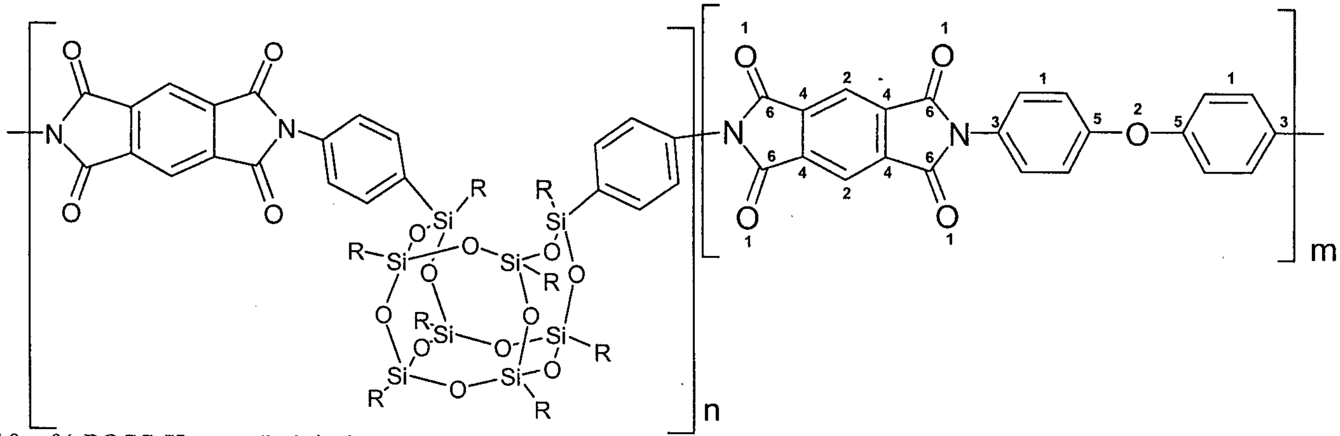
10 wt% POSS Kapton



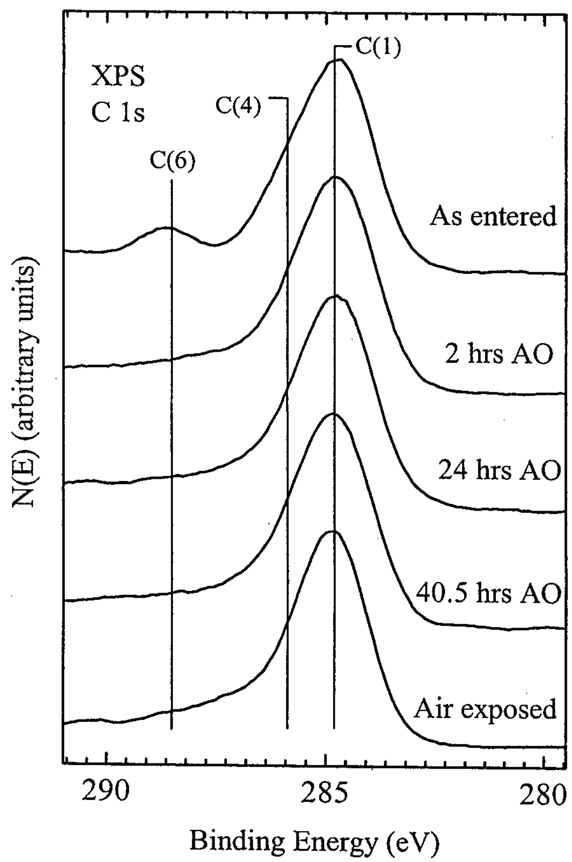


Composition, at %

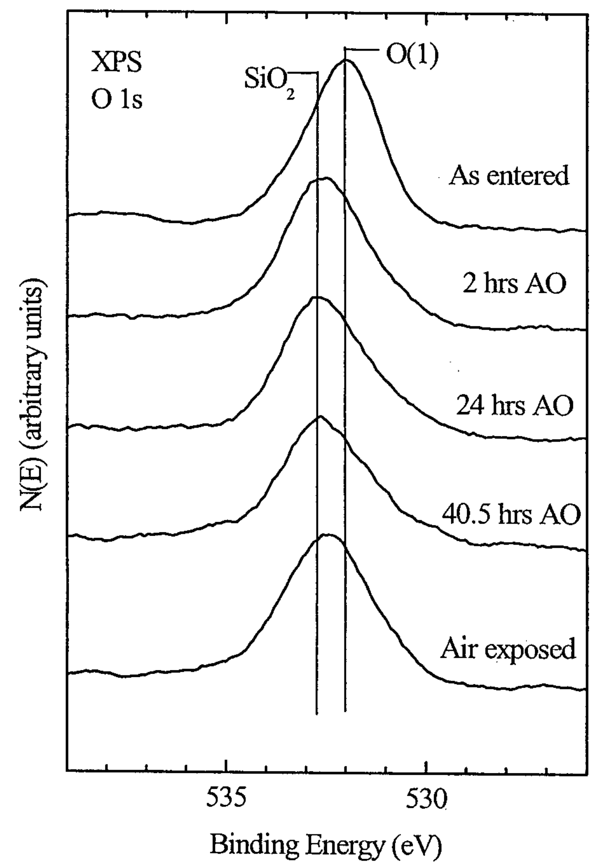
Sample Treatment	O	C	N	Si	O/Si
As entered	15.9	74.5	4.9	4.6	3.4
2.0-hr	14.3	72.6	8.2	4.9	2.9
24.0-hr	11.1	79.6	4.9	4.4	2.5
40.0-hr	9.1	81.5	5.6	3.7	2.4
Air exposed	13.9	76.8	5.8	3.5	3.9

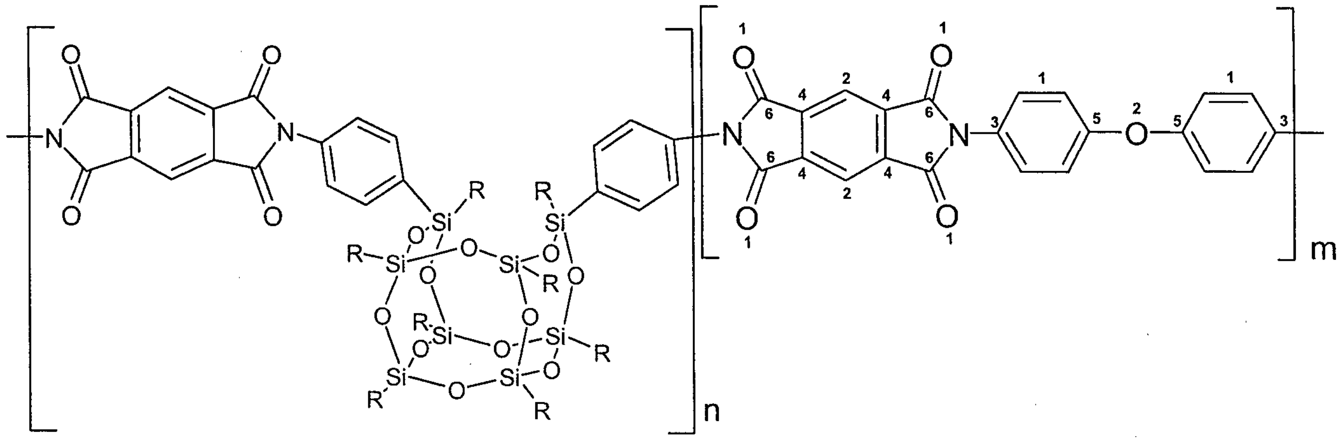


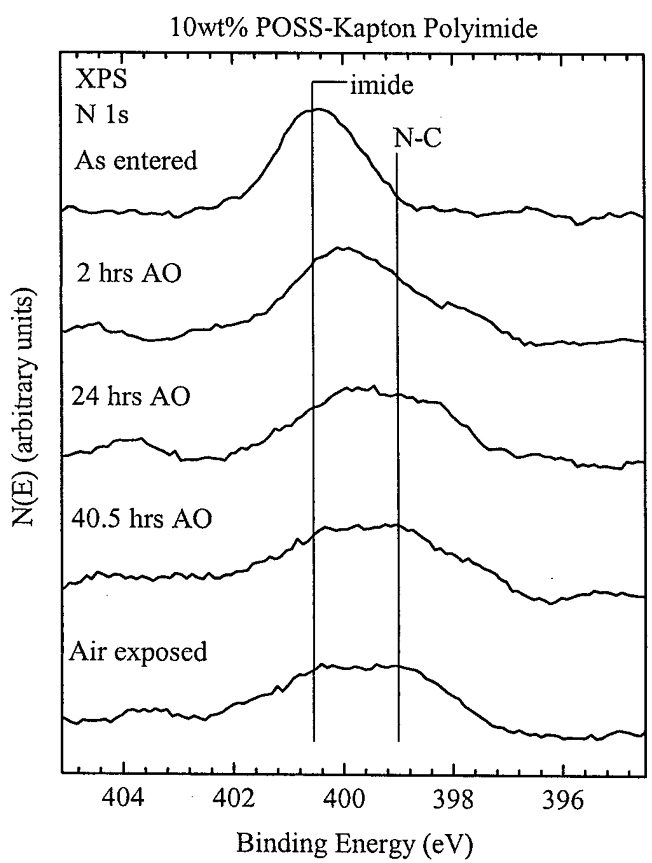
10wt% POSS-Kapton Polyimide



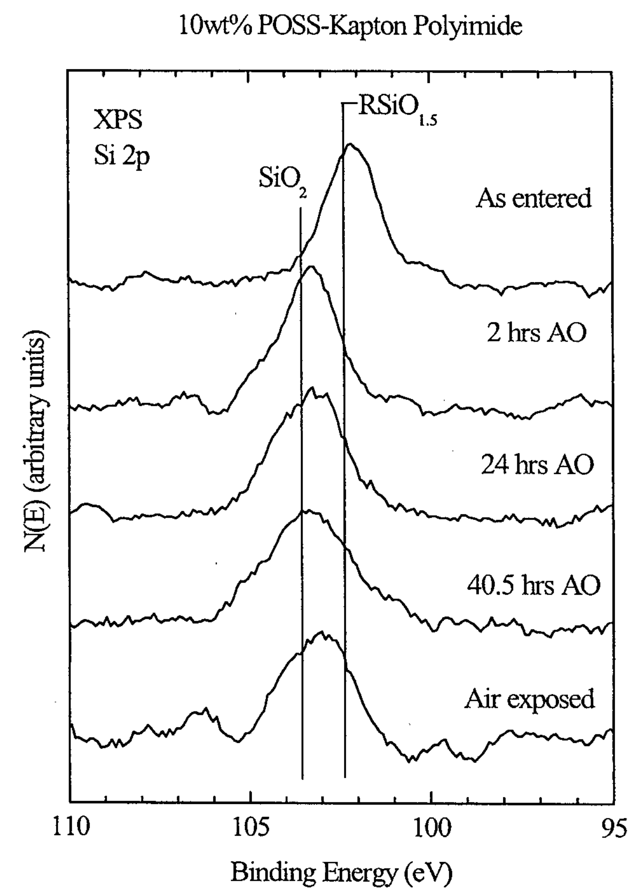
10wt% POSS-Kapton Polyimide





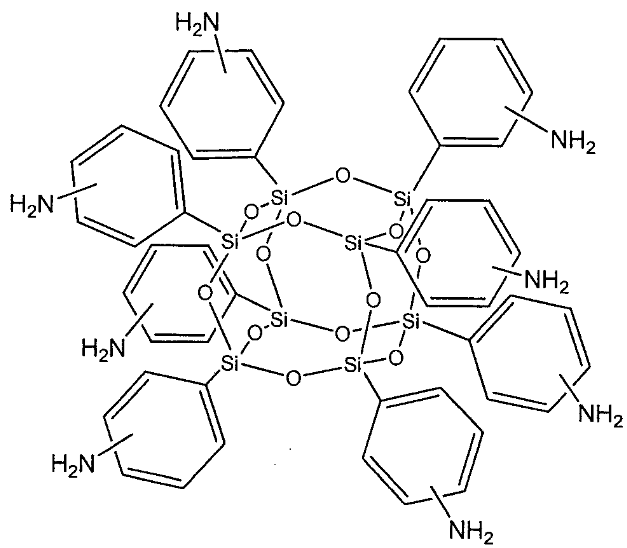


10wt% POSS-Kapton Polyimide
XPS
N 1s
imide
N-C
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
404
402
400
398
396
Binding Energy (eV)

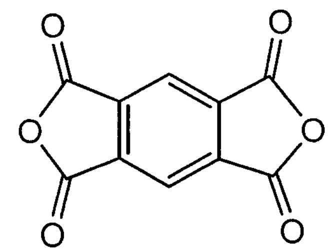


10wt% POSS-Kapton Polyimide
XPS
Si 2p
RSiO1.5
SiO2
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
110
105
100
95
Binding Energy (eV)

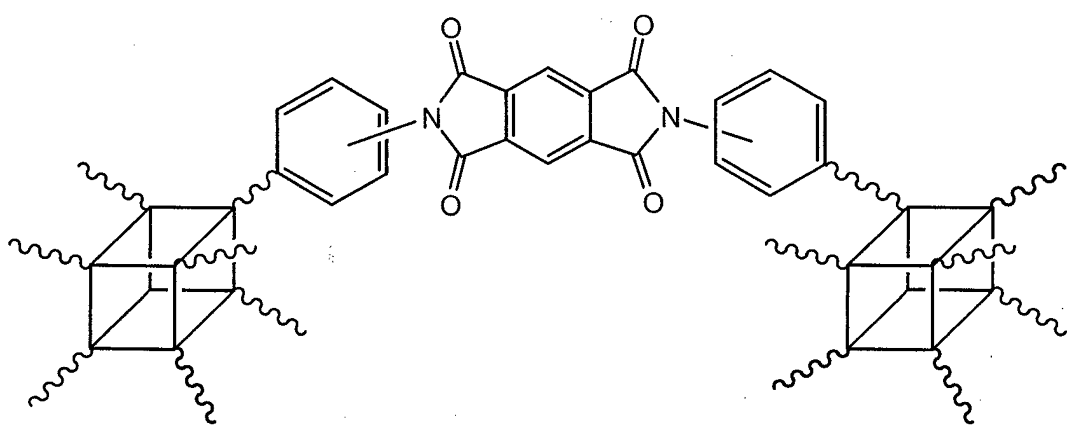
Octaphenylamino Silsesquioxane Imide Resin



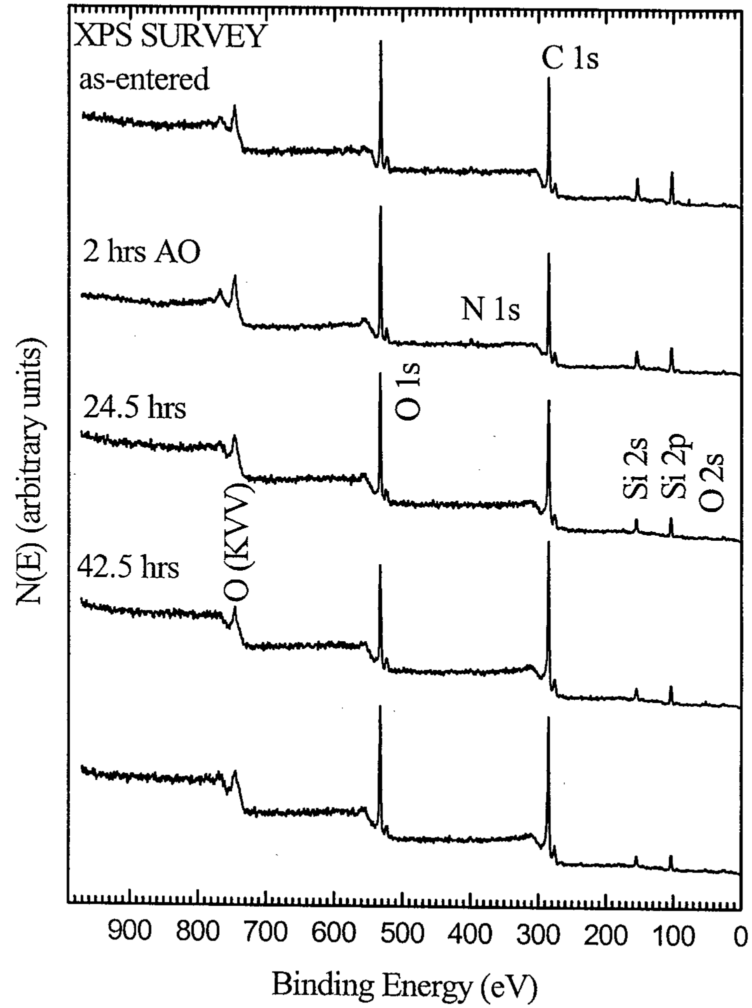
OAPS

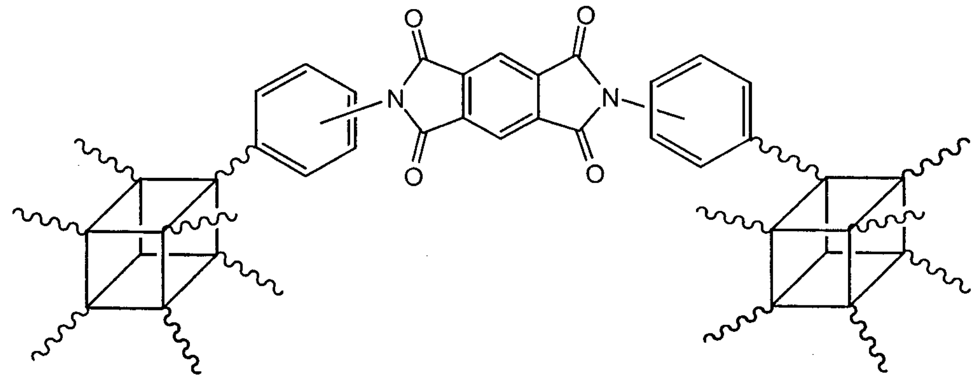


PMDA



Octaphenylamino Silsesquioxane Imide Resin

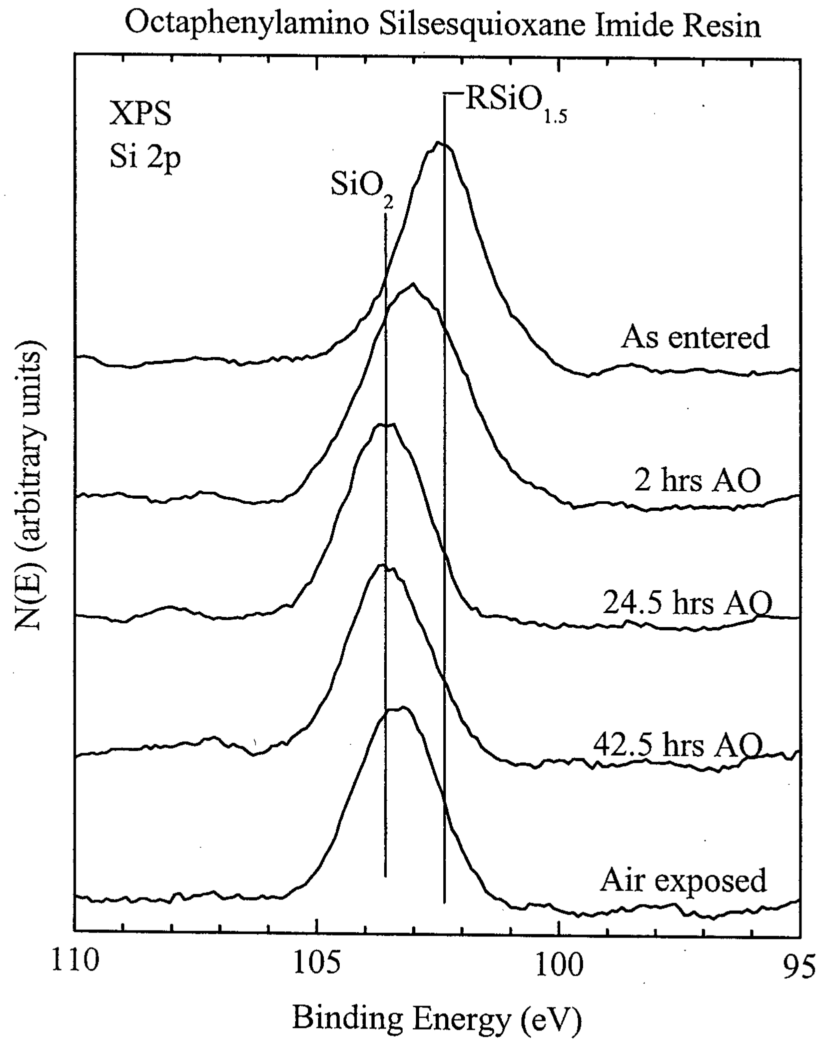


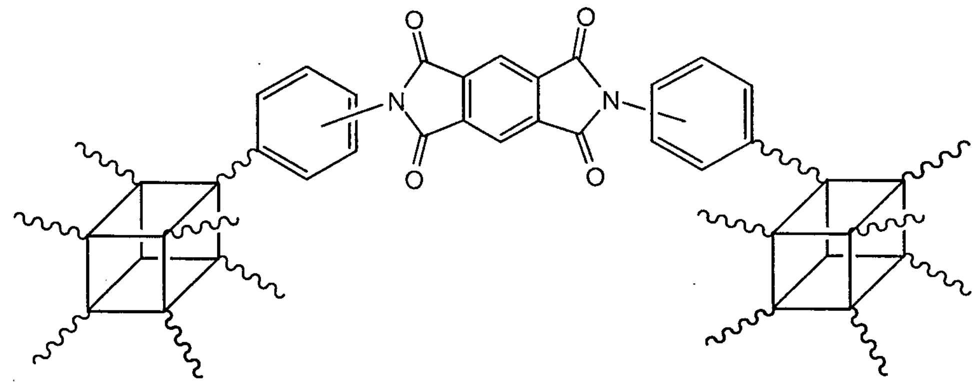


Composition, at %

Sample Treatment	O 1s	C1s	N 1s	Si 2p	O/Si
as entered	18.1	60.5	1.7	19.7	0.9
2hrs	22.8	57.1	2.1	18.0	1.3
24.5hrs	18.7	67.9	1.1	12.3	1.5
42.5hrs	16.2	71.3	2.4	10.1	1.6
Air exposed	19.3	71.5	0.9	8.3	2.3

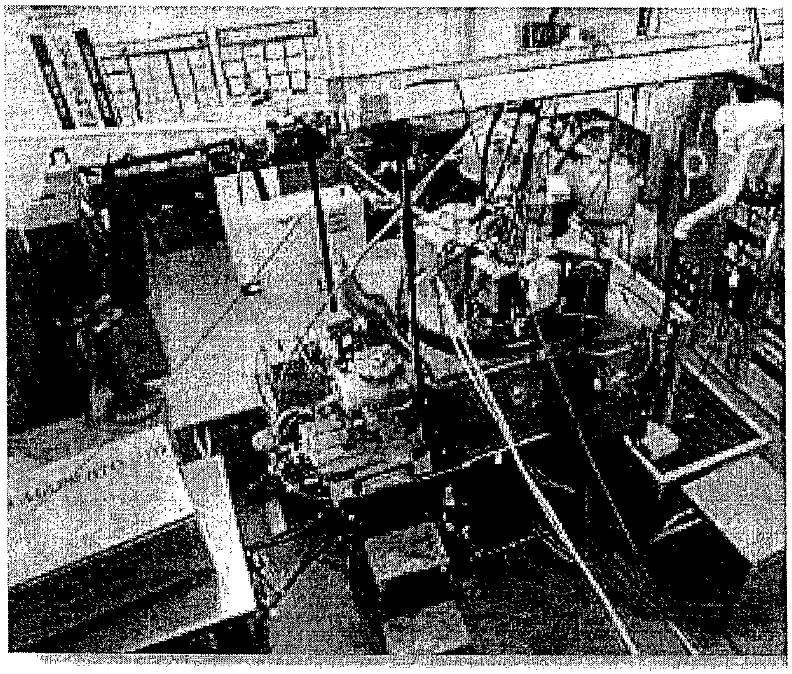
Octaphenylamino Silsesquioxane Imide Resin

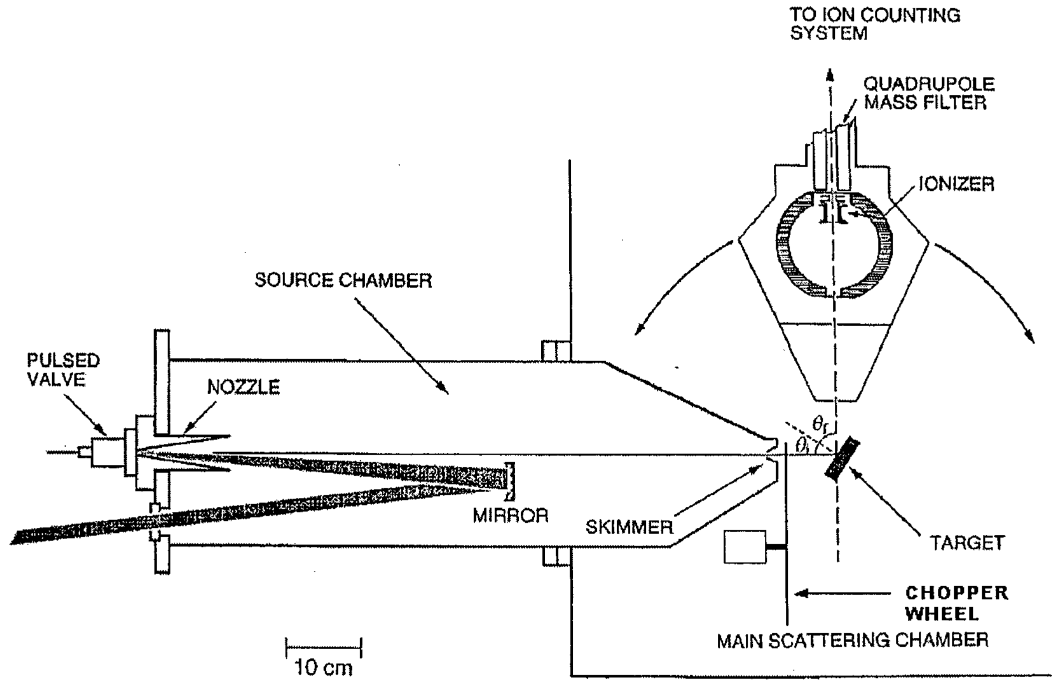




Montana State University Bozeman

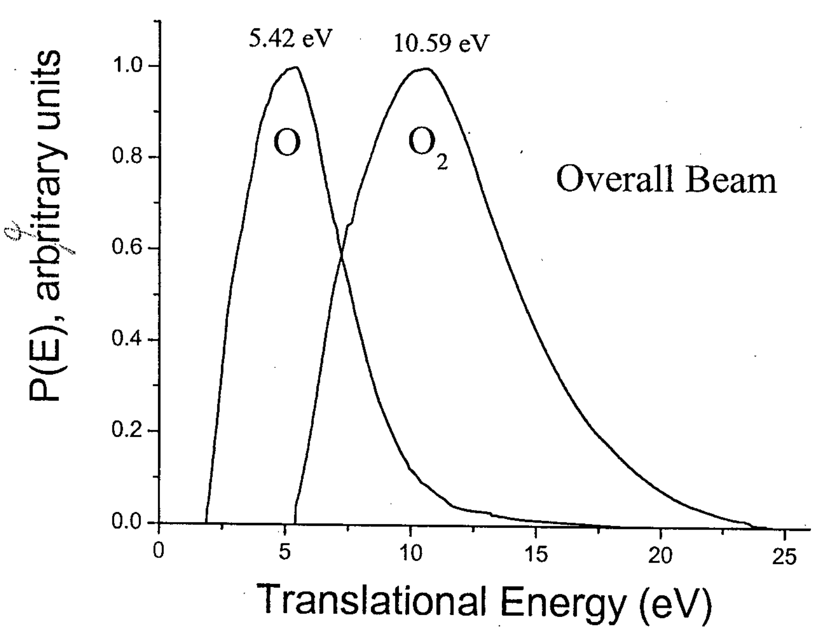
Beam-Surface Scattering/Atomic Oxygen Test Facility

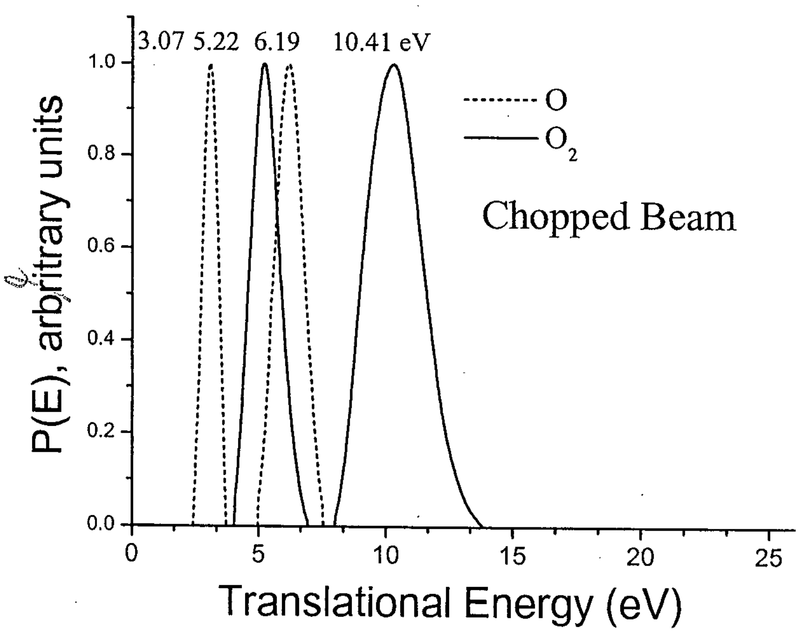




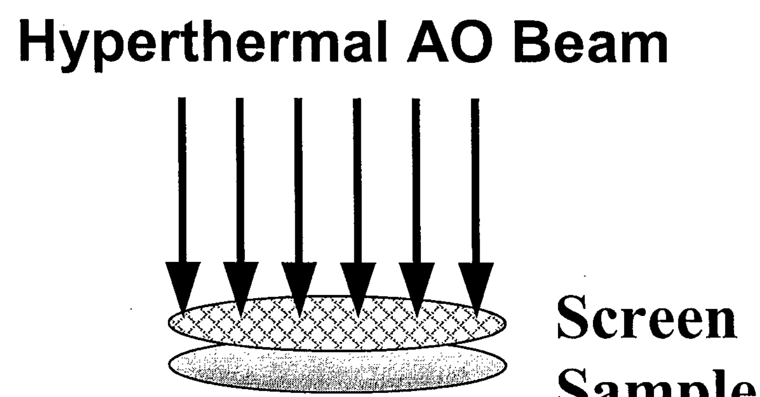
Pulsed CO_2 Laser Atomic Oxygen Generator

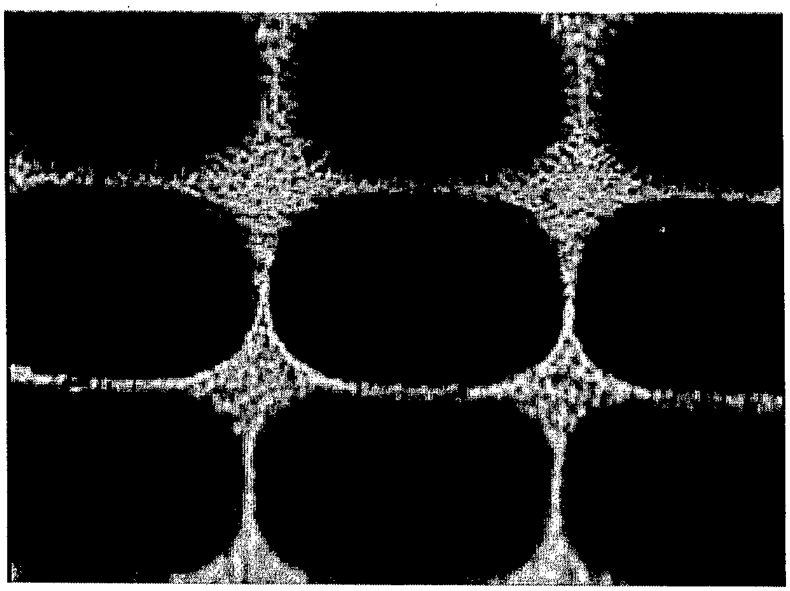
Energy distribution beams produced by the pulsed CO_2 laser AO source



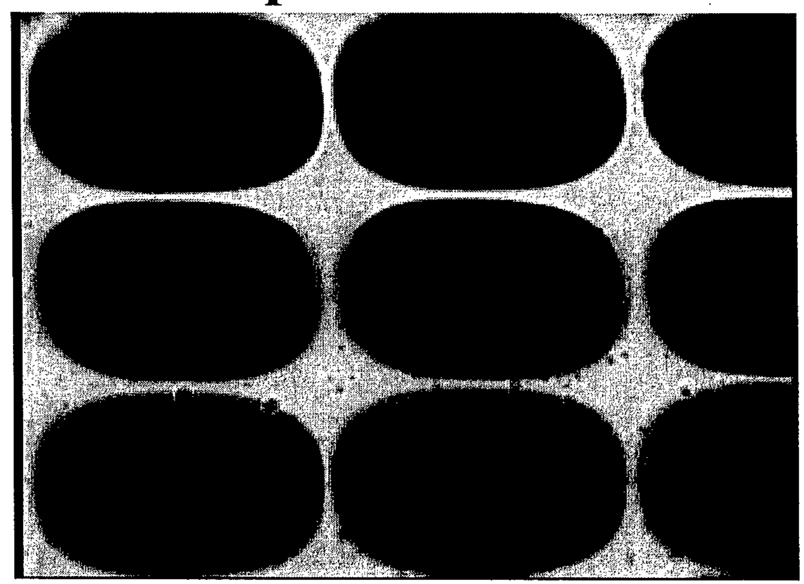


Surface Topographical Analysis/Profilometry





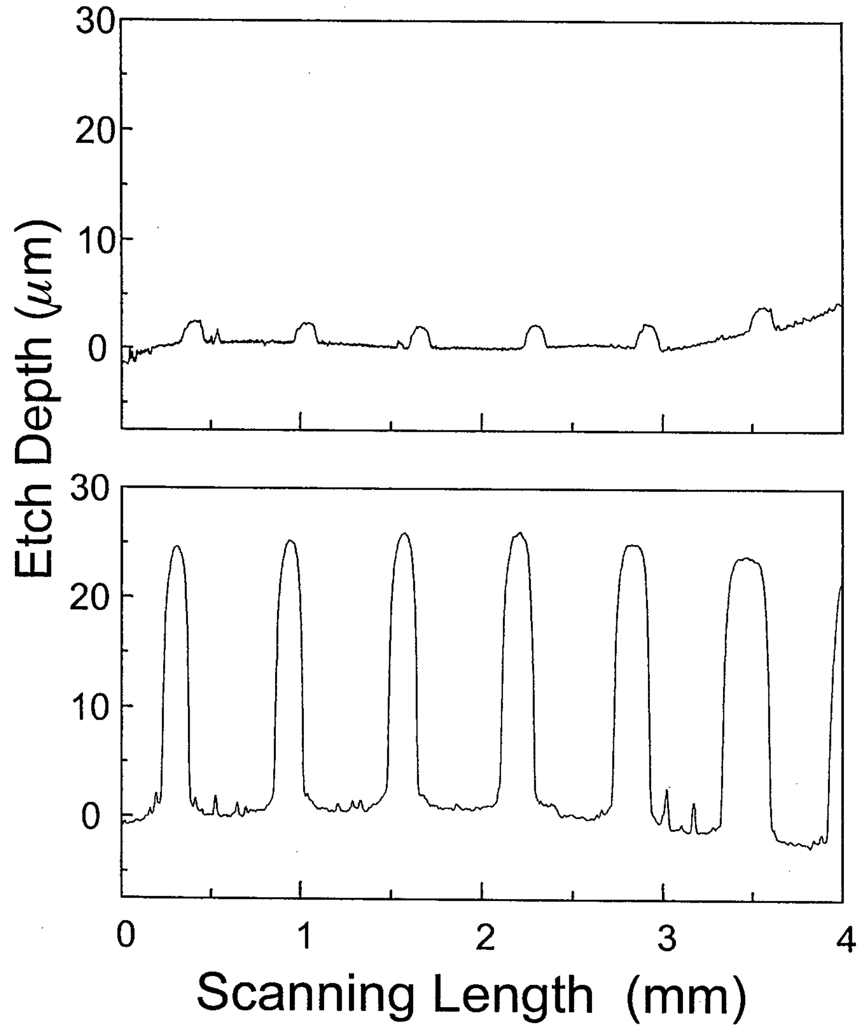
Kapton H



Kapton 10 wt% POSS

O-Atom Etching Experiment

8.47×10^{20} atoms cm^{-2}



Kapton 10 wt% POSS

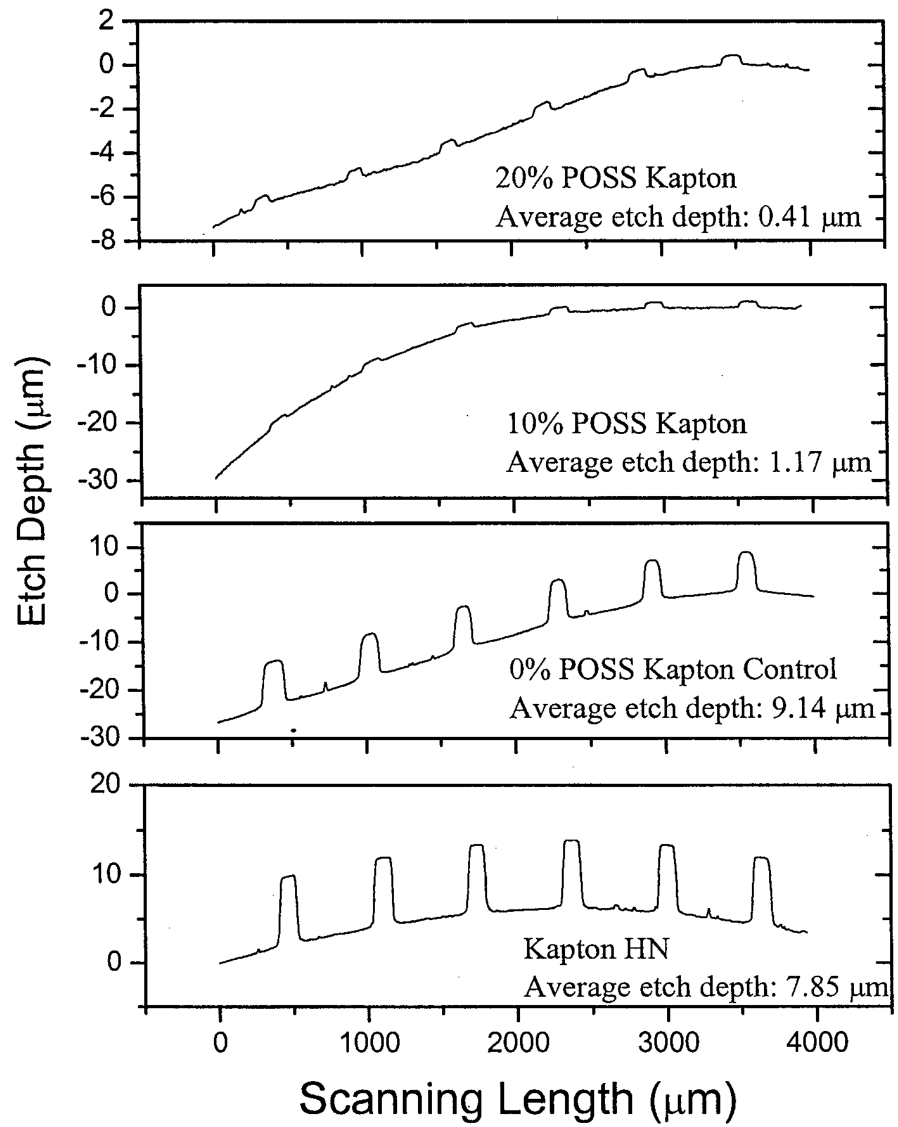
$R_e = 2.56 \times 10^{-25}$

Average etch depth:
2.2 μm

Kapton H Standard

$R_e = 3.00 \times 10^{-24}$

Average etch depth:
25.4 μm



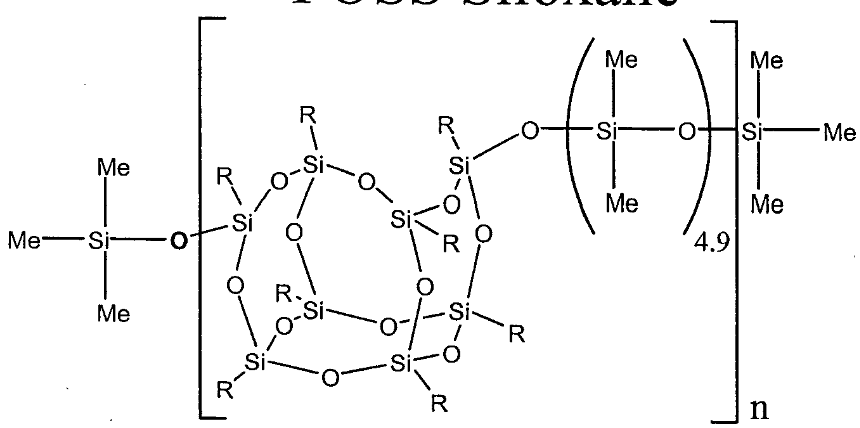
Multiplot of profilometry measurements obtained from Kapton HN and 0, 10 and 20 wt% POSS-Kapton polyimides exposed to a total AO fluence of 2.62×10^{20} atoms/cm^2.

O-Atom Etching Experiment

Total Fluence = 2.62×10^{20} atoms cm^{-2}

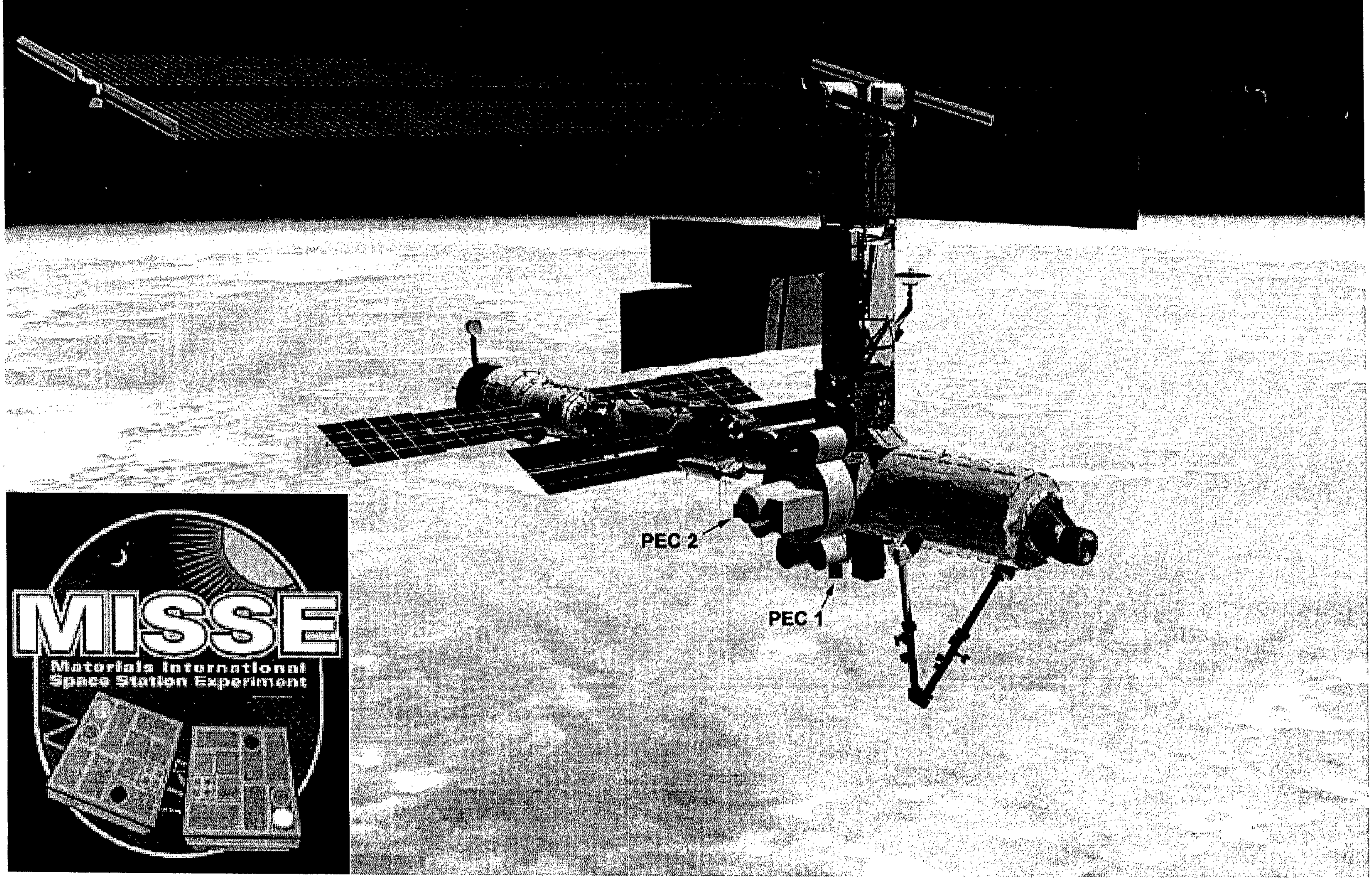
Sample	Kapton H	0% Poss Kapton Control	10%Poss Kapton	20%Poss Kapton	20% POSS-Polyurethane
Avg Etch Depth (microns)	7.85	9.14	1.15	0.41	6.05
Std Deviation	0.05	0.18	0.07	0.07	0.27
Re cm^3/atom	3.00E-24	3.49E-24	4.39E-25	1.55E-25	2.31E-24

POSS Siloxane



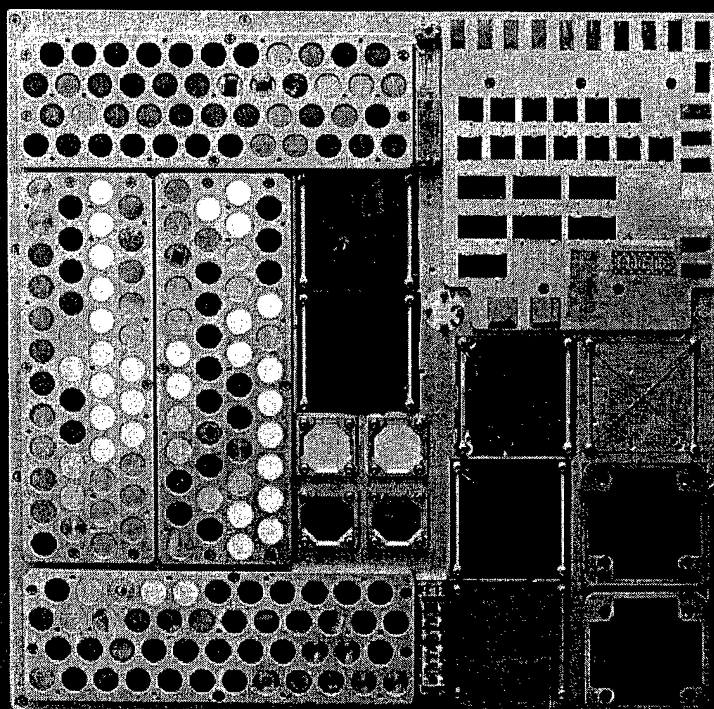
No erosion detected for POSS-Siloxane copolymer

MATERIALS INTERNATIONAL SPACE STATION EXPERIMENT



MATERIALS INTERNATIONAL SPACE STATION EXPERIMENT

1 YEAR AO & SOLAR
TRAY IN PEC 1 - TRAY 1

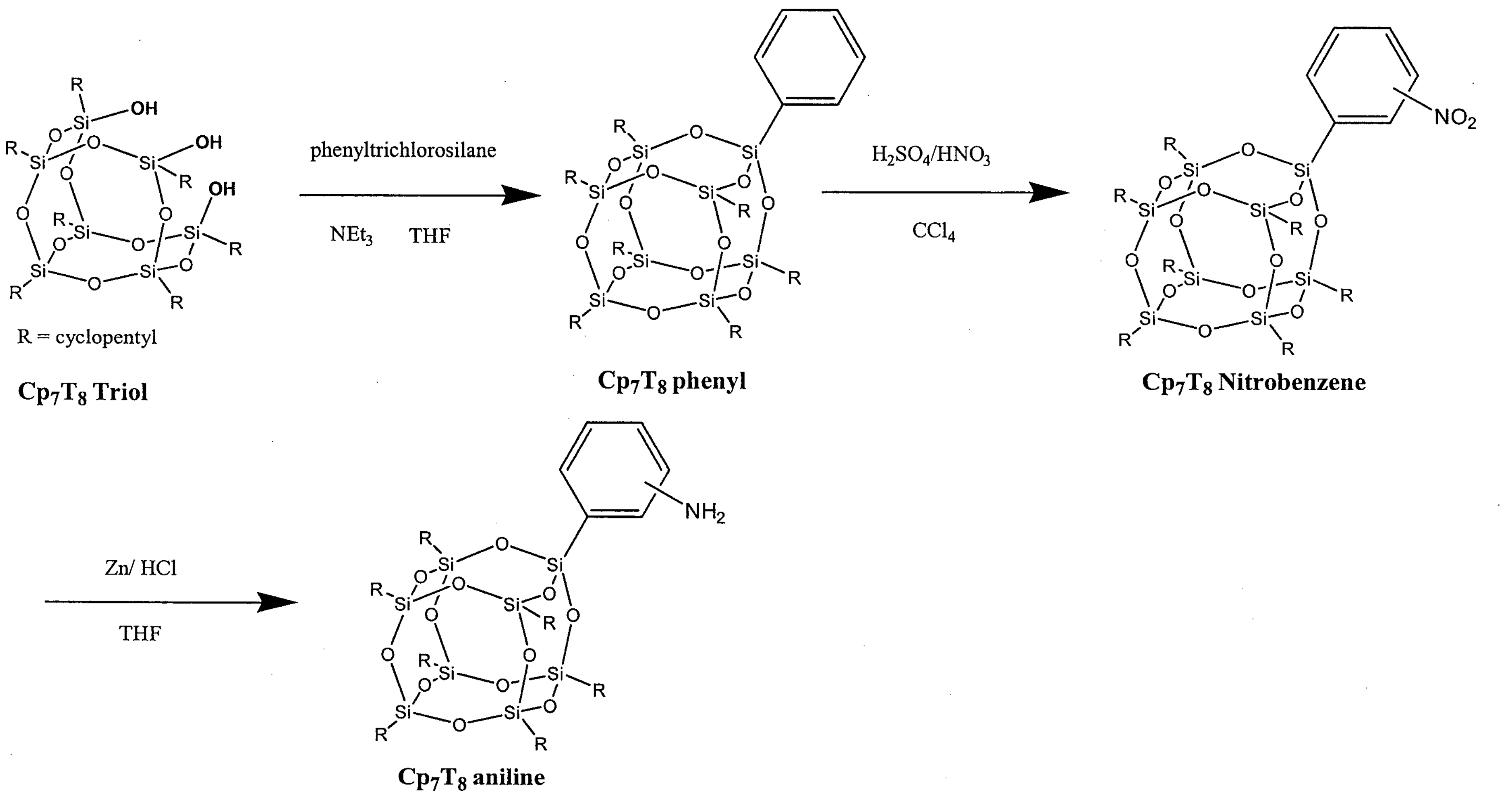


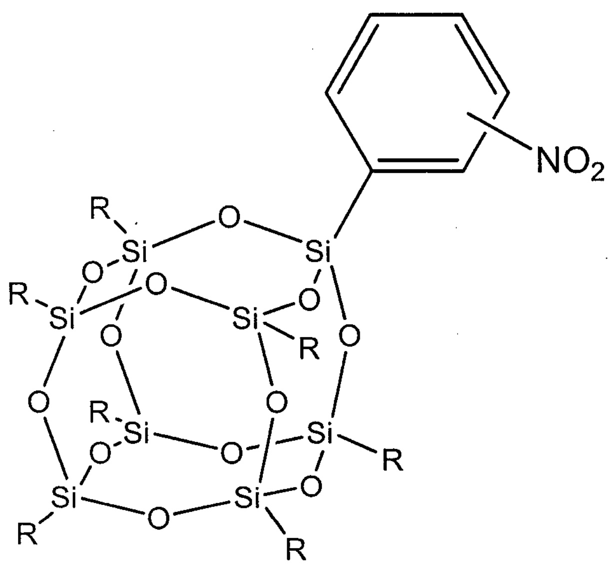
POSS in Space

POSS-Polymers Fly on STS 105 Discovery and are deployed on the Int'l Space Station 16 August 2001

Footage courtesy of NASA

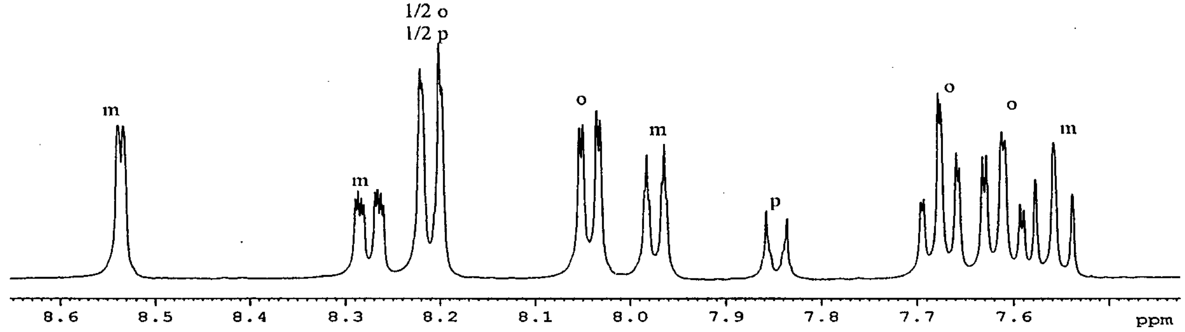
Development of CpPOSS aniline model compound

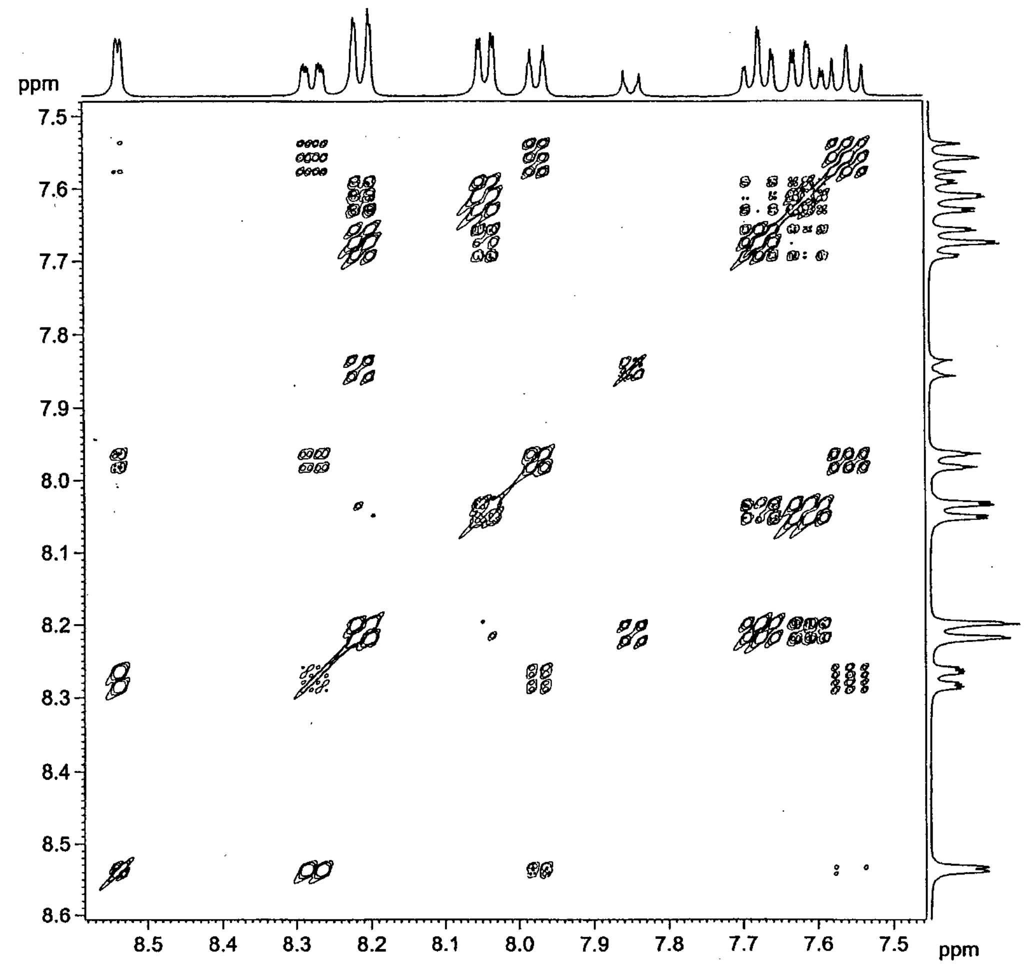


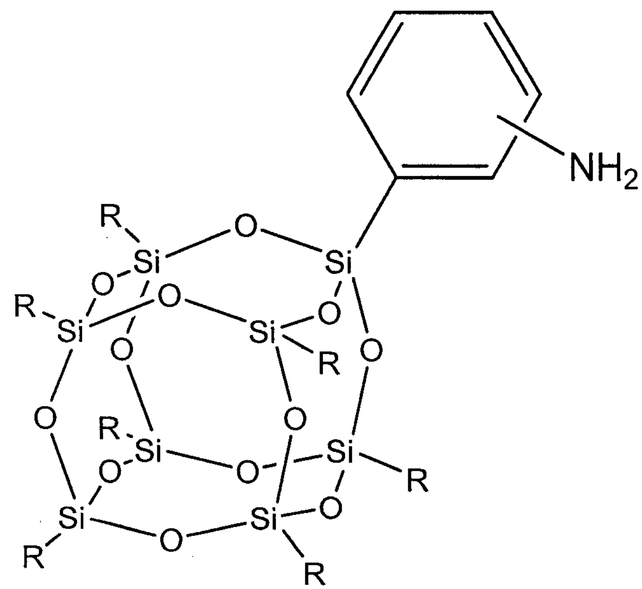


Cp_7T_8 Nitrobenzene

55% ortho
37 % meta
8% para





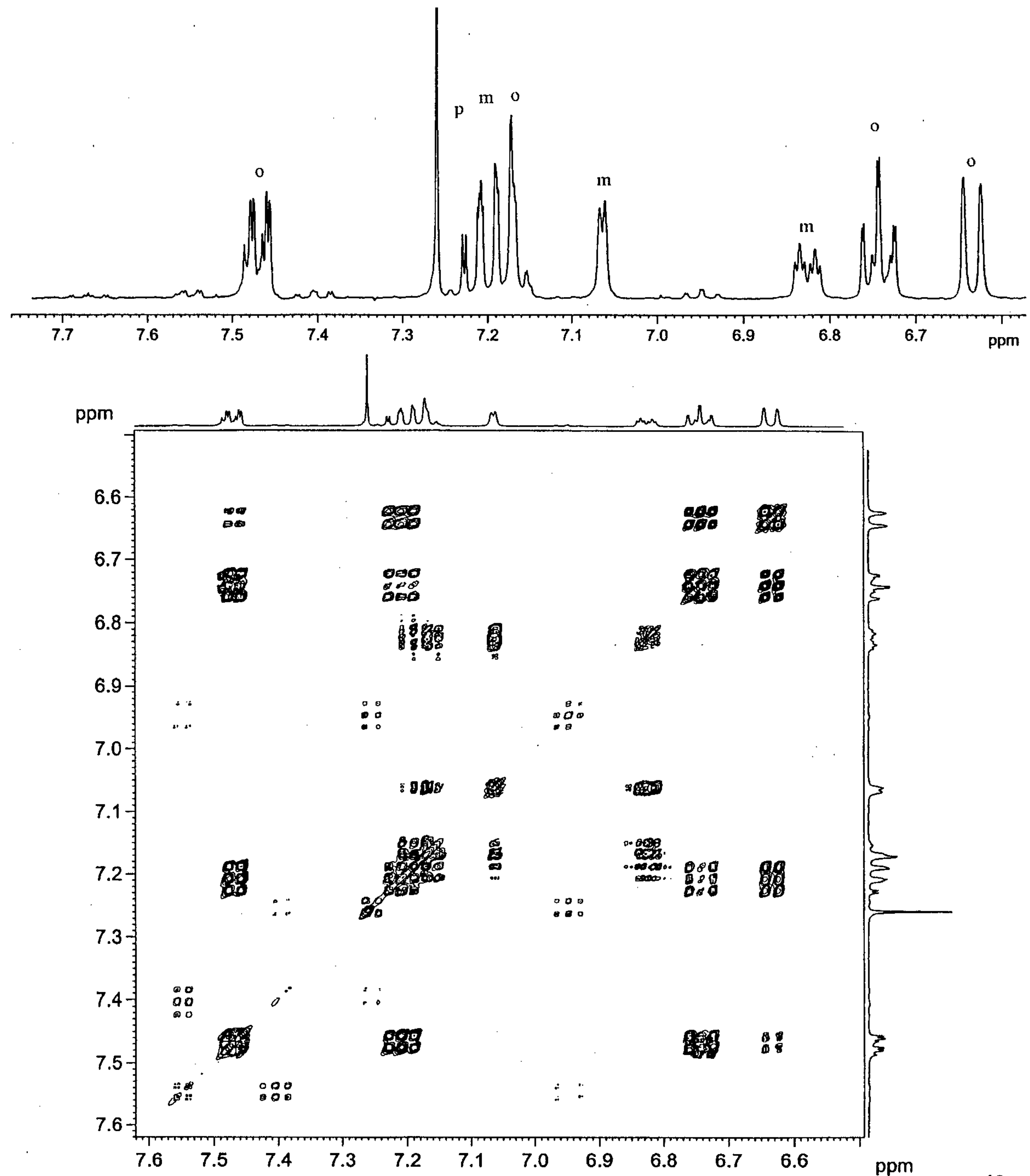


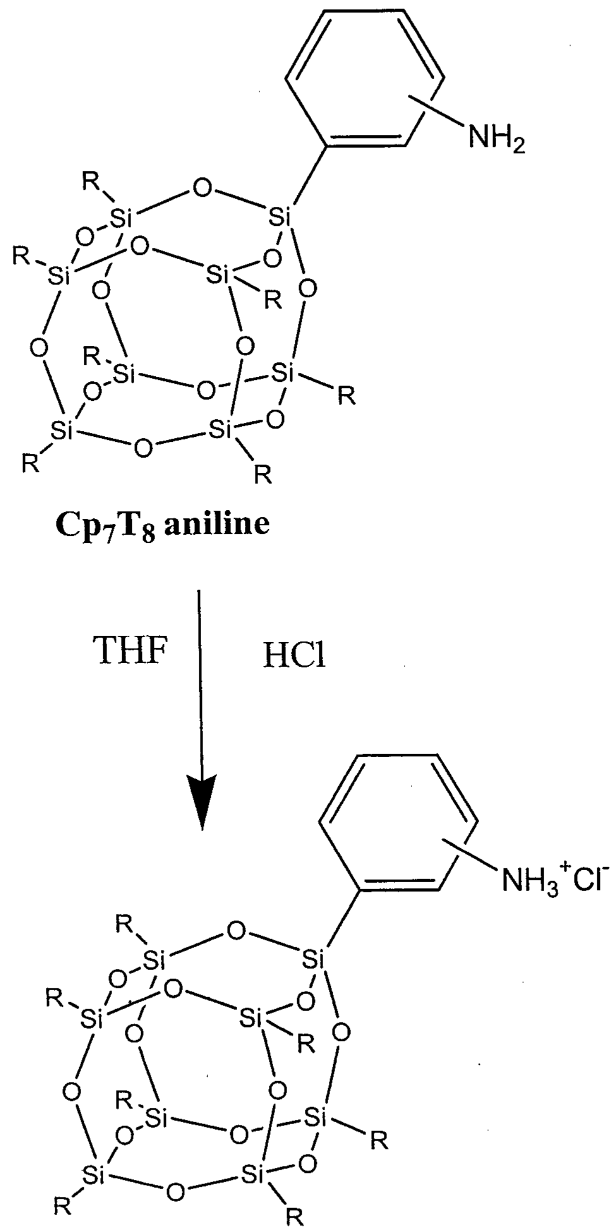
Cp_7T_8 aniline

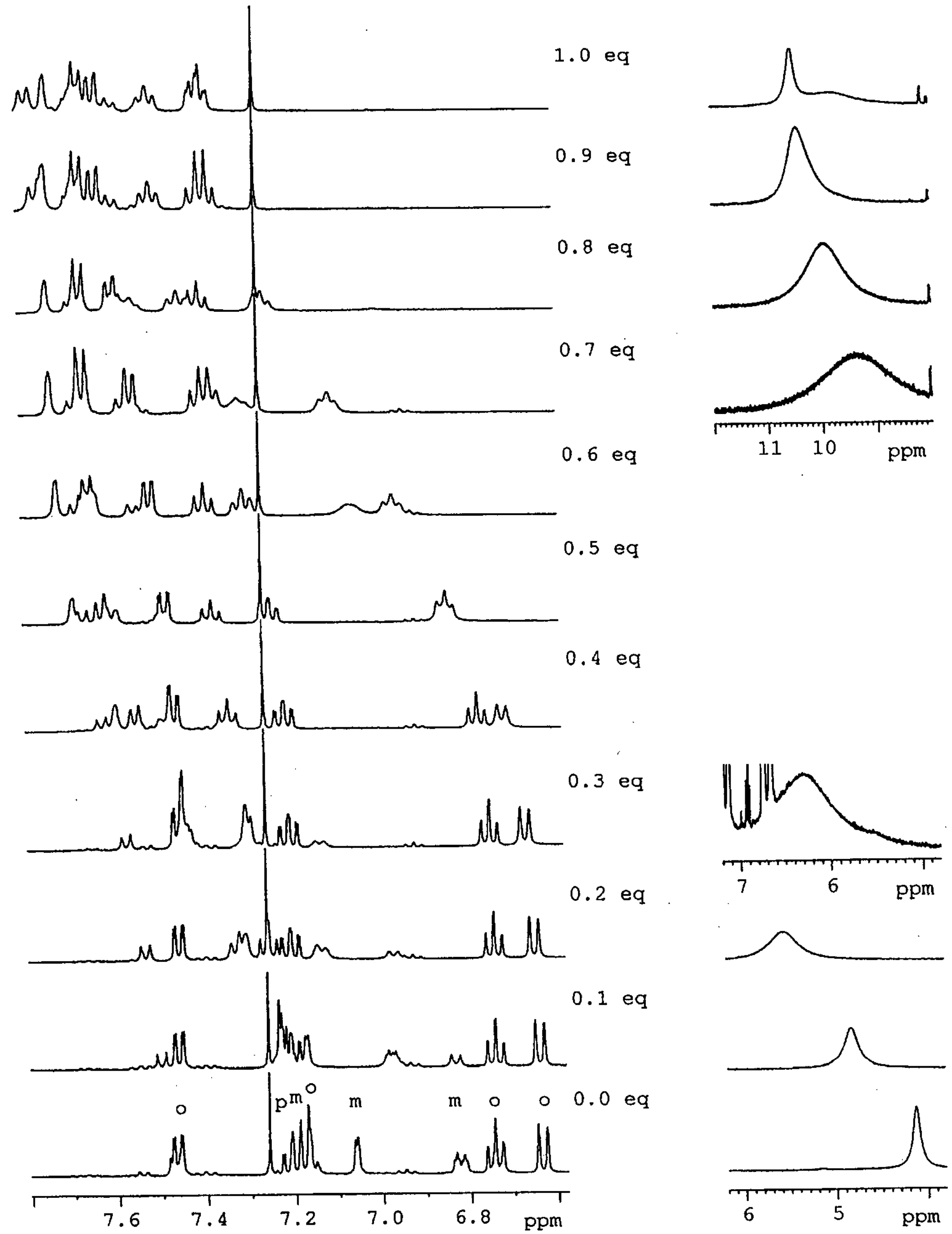
57% ortho

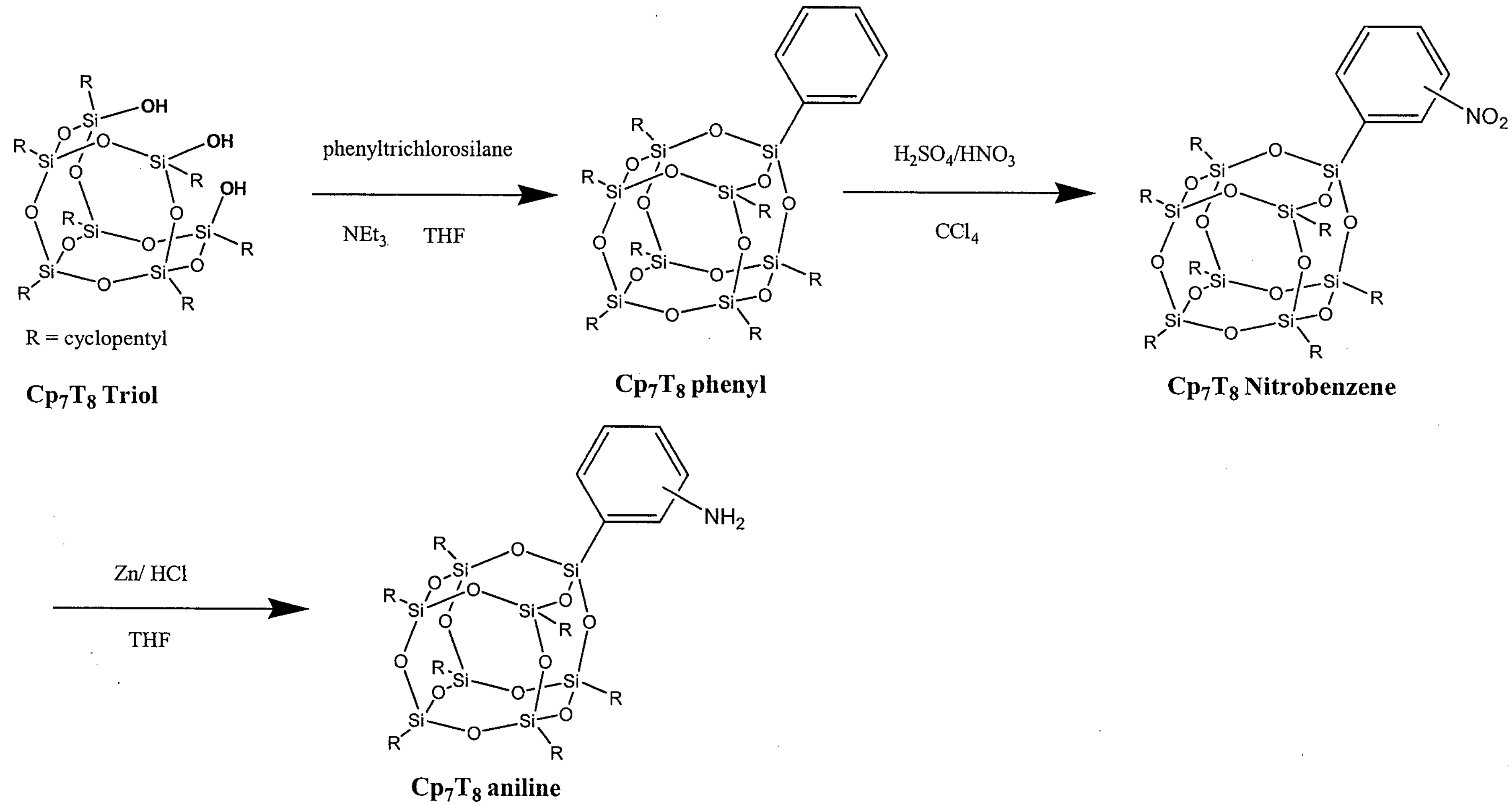
38 % meta

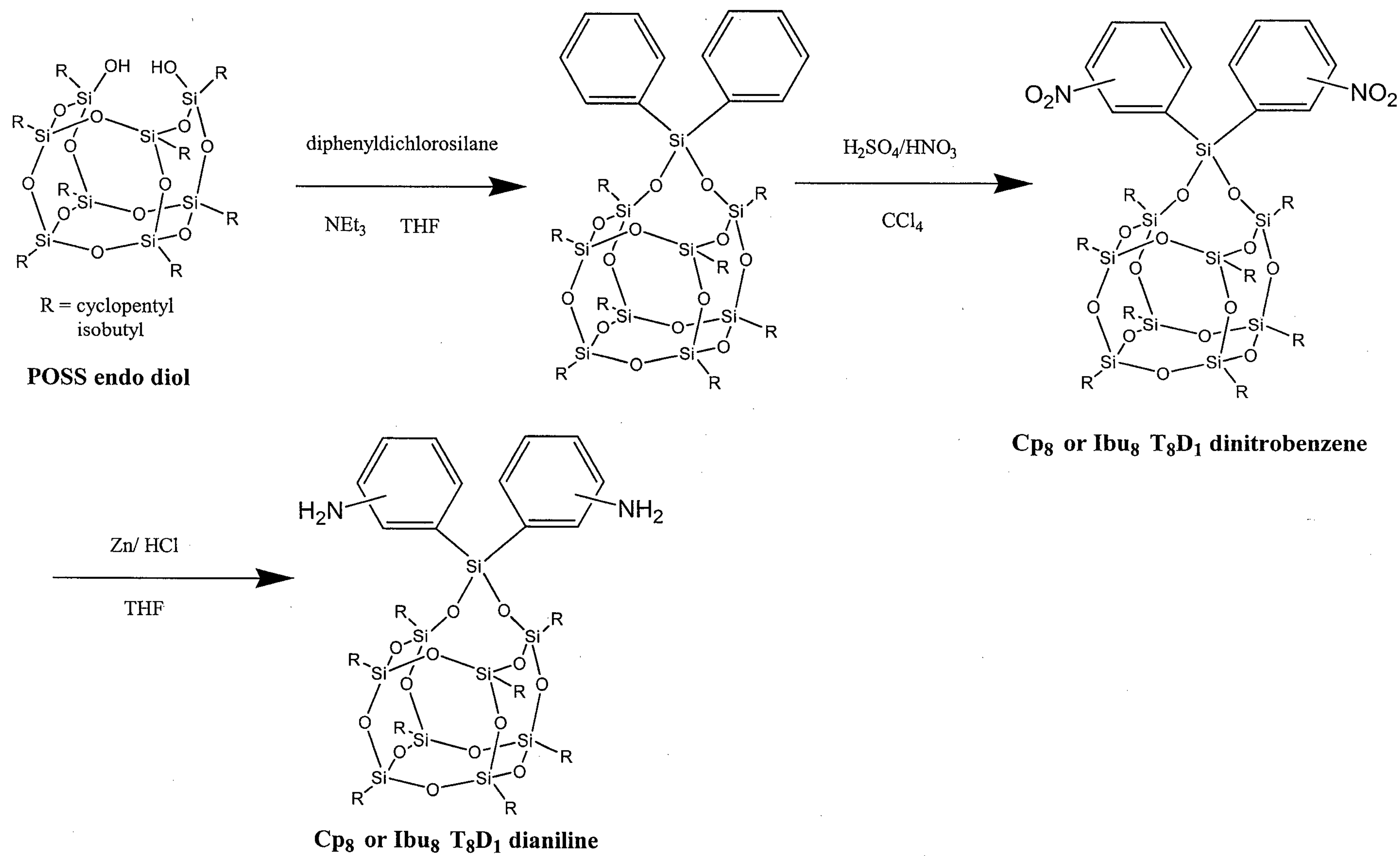
5% para




NH2
Cp7T8 aniline
THF
HCl
NH3+Cl-
R
Si
O


1.0 eq
0.9 eq
0.8 eq
0.7 eq
0.6 eq
0.5 eq
0.4 eq
0.3 eq
0.2 eq
0.1 eq
0.0 eq
o
p m o
m
m o o
7.6 7.4 7.2 7.0 6.8 ppm
11 10 ppm
7 6 ppm
6 5 ppm


R = cyclopentyl
Cp_7T_8 Triol
phenyltrichlorosilane
NEt_3 THF
Cp_7T_8 phenyl
H_2SO_4/HNO_3
CCl_4
Cp_7T_8 Nitrobenzene
Zn/ HCl
THF
Cp_7T_8 aniline



R = cyclopentyl
isobutyl
POSS endo diol
diphenyldichlorosilane
NEt3 THF
H2SO4/HNO3
CCl4
O2N
NO2
Cp8 or Ibu8 T8D1 dinitrobenzene
Zn/ HCl
THF
H2N
NH2
Cp8 or Ibu8 T8D1 dianiline

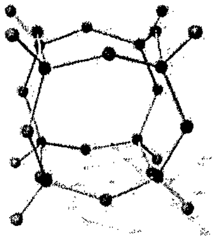
Future Work

- Synthesis of other POSS-analine monomer. AFRL & HP

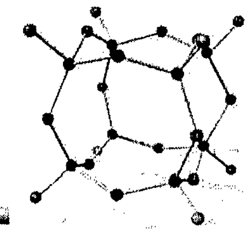
- Continue AO studies on other POSS-Polymer systems at UF
    - VUV Radiation with and without AO.
    - In-Situ Characterization XPS FTIR
    - Exposure to Different Gases
    - Sputtering Effects using FABS
    - Temperature Effects

- AO Etching and Profilometry Experiments at MSU

- VUV, Proton and Electron Radiation at Aerospace



Acknowledgements



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AFRL